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(71) Applicant: **MICHIGAN STATE UNIVERSITY**
[US/US]; 238 Administration Building, East Lansing, MI
48824 (US).

(72) Inventors: **SMITH, Milton, R., III**; 238 Oxford Road,
East Lansing, MI 48823 (US). **MALECZKA, Robert, E.**;
13420 Tucker Drive, Dewitt, MI 48820 (US).

(74) Agent: **MCLEOD, Ian, C.**; McLeod & Moyne P.C., 2190
Commons Parkway, Okemos, MI 48864 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
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GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE CATALYTIC SYNTHESIS OF BIARYLS AND POLYMERS FROM ARYL COMPOUNDS

(57) Abstract: A process for producing organic substituted aromatic or heteroaromatic compounds including biaryl and biheteroaryl compounds in a two-step reaction. In the first step, the aromatic or heteroaromatic compound is borylated in a reaction comprising a borane or diborane reagent (any boron reagent where the boron reagent contains a B-H, B-B or B-Si bond) and an iridium or rhodium catalytic complex. In the second step, a metal catalyst catalyzes the formation of the organic substituted aromatic or heteroaromatic compound from the borylated compound and an electrophile such as an aryl or organic halide, triflate (OSO₂CF₃), or nonaflate (OSO₂C₄F₉). The steps in the process can be performed in a single reaction vessel or in separate reaction vessels. The present invention also provides a process for synthesis of complex polyphenylenes starting from halogenated aromatic compounds.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/22430

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C07C 22/00, 25/13, 17/00, 25/00

US CL :570/143, 144, 190, 201

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 570/143, 144, 190, 201

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN, EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,976,596 A (HAWTHORNE ET AL.) 24 August 1976 (24.08.1976), entire document.	1-34, 36-49
A	US 5,763,688 A (IKARIYA ET AL.) 9 June 1998 (09.06.1998), entire document.	1-34, 36-49
A	US 5,831,117 A (NG ET AL.) 3 November 1998 (03.11.1998), entire document.	1-34, 36-49
A	US 6,184,381 B1 (IKARIYA ET AL.) 6 February 2001 (06.02.2001), entire document.	1-34, 36-49

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

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Date of mailing of the international search report

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 Washington, D.C. 20231

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Form PCT/ISA/210 (second sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No.

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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 35
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

There is no Claim 35 in this application.
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

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- (72) Inventor: SMITH, Milton, R., III; 238 Oxford Road, East
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- (74) Agent: MCLEOD, Ian, C.; McLeods & Moyne, P.C.,
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- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: CATLAYTIC BORONATE ESTER SYNTHESIS FROM BORON REAGENTS AND HYDROCARBONS

(57) Abstract: A process for producing a ring-substituted arene borane which comprises reacting a ring-substituted arene with an HB organic compound in the presence of a catalytically effective amount of an iridium or rhodium complex with three or more substituents, excluding hydrogen, bonded to the iridium or rhodium and a phosphorus organic ligand, which is at least in part bonded to the iridium or rhodium, to form the ring-substituted arene borane. Also provided are catalytic compounds for catalyzing the process comprising an iridium or rhodium complex with three or substituents, excluding hydrogen, bonded to the iridium or rhodium and optionally, a phosphorus organic ligand, which is at least in part bonded to the iridium or rhodium.

CATALYTIC BORONATE ESTER SYNTHESIS
FROM BORON REAGENTS AND HYDROCARBONS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority to Provisional Application No. 60/305,107, filed July 13, 2001.

5

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT

This invention was supported in part by National Institutes of Health, National Institute of
10 General Medical Sciences Grant No. R01 GM63188-01 and
in part by National Science Foundation Grant No. CHE-
9817230. The U.S. government has certain rights in
this invention.

15 Reference to a "Computer Listing Appendix submitted on
a Compact Disc"

Not Applicable.

BACKGROUND OF THE INVENTION

20

(1) Field of the Invention

The present invention relates to a process
for producing a ring-substituted arene borane which
comprises reacting a ring-substituted arene with an HB
25 organic compound in the presence of a catalytically
effective amount of an iridium or rhodium complex with
three or more substituents, excluding hydrogen, bonded
to the iridium or rhodium and a phosphorus organic
ligand, which is at least in part bonded to the

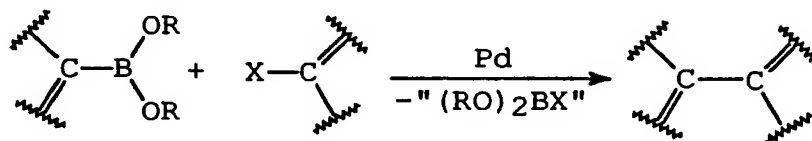
iridium or rhodium, to form the ring-substituted arene borane. The present invention further relates to compounds for catalyzing the process comprising an iridium or rhodium

- 5 complex with three or substituents, excluding hydrogen, bonded to the iridium or rhodium and optionally, a phosphorus organic ligand, which is at least in part bonded to the iridium or rhodium.

10 (2) Description of Related Art

Alkyl and arylboronic esters and acids are versatile alkyl and aryl transfer reagents in organic chemistry wherein the boron serves as a "mask" for a broad range of heteroatoms and functional groups.

- 15 Some of the most remarkable and broadly used applications of organoboron chemistry are catalytic cross-coupling reactions of C-B and C-X (X= Cl, Br, or I) groups which yield new C-C bonds as shown below.



20

In the pharmaceutical industry, organoboron complexes are key building blocks for drug manufacturing, versatile reagents for high-throughput parallel synthesis in drug discovery, and exhibit some useful

- 25 and unique biological activities.

Arylboronate esters and the corresponding acids are presently prepared by reacting Grignard reagents generated from halogenated aromatics and magnesium metal with alkyl borate reagents. A related
30 method involves the reaction of alkyllithium reagents

with aromatic halides or arenas to generate lithium reagents which are subsequently reacted with alkyl borates. Significant limitations of the current technologies include: (1) the reactions are run in
5 ethereal solvents, (2) halogenated aromatics must be synthesized from hydrocarbon feedstocks, (3) for large-scale synthesis, unreacted chlorinated aromatic starting materials and biaryl byproducts can create significant environmental hazards and pose waste
10 disposal problems, (4) in some instances attempted product isolation has resulted in explosions attributed to unreacted lithium and magnesium intermediates, (5) Grignard and organolithium reagents can be incompatible with a range of common functional
15 groups including esters, amides, bromides, chlorides, iodides, alcohols, acids, and the like, and (6) cryogenic cooling is sometimes required to prevent side reactions.

In light of the above limitations of the
20 current processes for producing boronate esters and acids, there remains a need for a general synthetic route to synthesizing boronate esters and acids which does not have the limitations of the current processes.

25

SUMMARY OF THE INVENTION

The present invention provides a catalytic composition comprising an iridium or rhodium complex with three or more substituents, excluding
30 hydrogen, bonded to the iridium or rhodium. In a further embodiment, the present invention provides a catalytic composition comprising an iridium or rhodium

complex with three or more substituents, excluding hydrogen, bonded to the iridium or rhodium and a ligand selected from the group consisting of a phosphorus organic ligand, an organic amine, an imine,
5 a nitrogen heterocycle, and an ether in a molar ratio between about 1 to 3 and 1 to 1, wherein the ligand is at least in part bonded to the iridium or rhodium.

In a preferred embodiment of the present invention, the phosphorus organic ligand is selected
10 from the group consisting of trimethyl phosphine (PMe_3), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,2-bis(diphenylphosphino)ethane (dppe).

In a further embodiment of the catalytic composition, the iridium complex is $(\text{ArH})\text{Ir}(\text{BY})_3$
15 wherein ArH is selected from the group consisting of aromatic, heteroaromatic, polyaromatic, and heteropolyaromatic hydrocarbon; and BY is a boron moiety.

In a further embodiment of the catalytic
20 composition, the iridium complex is $(\text{MesH})\text{Ir}(\text{BY})_3$ wherein MesH is mesitylene; and BY is a boron moiety.

In a further embodiment of the catalytic composition, the iridium complex is $(\text{P}(\text{Y}_4)(\text{Y}_5)(\text{Y}_6))_3\text{Ir}(\text{H})_n(\text{BY})_{3-n}$ wherein Y_4 , Y_5 , and Y_6 are each selected from
25 the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-\text{O}(\text{R}_{11})$), and amide ($-\text{N}(\text{R}_{12})(\text{R}_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a
30 carbon in a cyclic structure; n is 0, 1, or 2; and BY is a boron moiety.

In a further embodiment of the catalytic

composition, the iridium complex is $(P(R_{14})(R_{15})(R_{16}))_3Ir(H)_n(BY)_{3-n}$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; n is 0, 1, or 2; and BY is a boron moiety.

In a further embodiment of the catalytic composition, the iridium complex is $(P(Y_4)(Y_5)(Y_6))_3Ir(H)(R_{17})(BY)$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; R_{17} is selected from the group consisting of a linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure; and BY is a boron moiety.

In a further embodiment of the catalytic composition, the iridium complex is $(P(R_{14})(R_{15})(R_{16}))_3Ir(H)(R_{17})(BY)$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; R_{17} is selected from the group consisting of a linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure; and BY is a boron moiety.

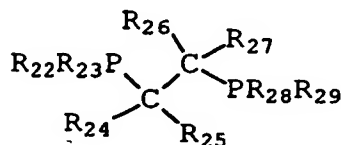
In a further embodiment of the catalytic composition, the iridium complex is $\{(PY_7P)Ir(BY)_3\}_2(\mu_2-(PY_7P))$ wherein BY is a boron moiety; (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected

from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12
5 carbons.

In a further embodiment of the catalytic composition, the iridium complex is $(PY_7P)(P(Y_4)(Y_5)(Y_6))Ir(BY)_3$ wherein BY is a boron moiety; Y_4 , Y_5 , and Y_6 are each selected from the group
10 consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon
15 in a cyclic structure; and (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is
20 a chain containing 1 to 12 carbons.

In a further embodiment of the catalytic composition, the iridium complex is $(PY_7P)(P(R_{14})(R_{15})(R_{16}))Ir(BY)_3$ wherein BY is a boron moiety; R_{14} , R_{15} , and R_{16} are each selected from the
25 group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl
30 containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

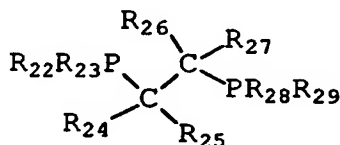
In a further embodiment of the catalytic composition, the iridium complex is $\{(P^{\sim}P)Ir(BY)_3\}_2(\mu_2-(P^{\sim}P))$ wherein BY is a boron moiety and wherein $(P^{\sim}P)$ is of the formula



5

wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

In a further embodiment of the catalytic composition, the iridium complex is $(P^{\sim}P)(P(Y_4)(Y_5)(Y_6))Ir(BY)_3$ wherein BY is a boron moiety; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and wherein $(P^{\sim}P)$ is of the formula

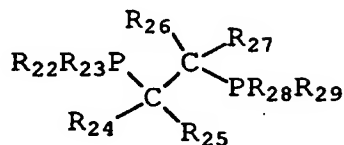


20

wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

In a further embodiment of the catalytic composition, the iridium complex is $(P^{\sim}P)(P(R_{14})(R_{15})(R_{16}))Ir(BY)_3$ wherein BY is a boron moiety; R_{14} , R_{15} , and R_{16} are each selected from the

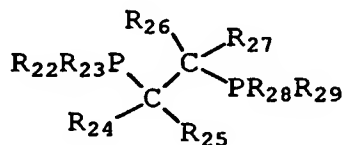
group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; and wherein (P[~]P) is of the formula



5 wherein R₂₂, R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈, and R₂₉ are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

In a further embodiment of the catalytic composition, the iridium complex is (PY₇P)Ir(BY)₃
 10 wherein BY is a boron moiety; and (PY₇P) is R₁₈R₁₉P-Y₇-PR₂₀R₂₁ wherein R₁₈, R₁₉, R₂₀, and R₂₁ are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic
 15 structure, and Y₇ is a chain containing 1 to 12 carbons.

In a further embodiment of the catalytic composition, the iridium complex is (P[~]P)Ir(BY)₃ wherein BY is a boron moiety and wherein (P[~]P) is of
 20 the formula



wherein R₂₂, R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈, and R₂₉ are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

25 In a further embodiment of the catalytic composition, the iridium complex is (P(Y₄)(Y₅)(Y₆))₄Ir(BY) wherein Y₄, Y₅, and Y₆ are each

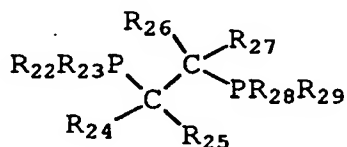
selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl
5 containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and BY is a boron moiety.

In a further embodiment of the catalytic composition, the iridium complex is
10 $(P(R_{14})(R_{15})(R_{16}))_4Ir(BY)$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; and BY is a boron moiety.

In a further embodiment of the catalytic
15 composition, the iridium complex is $(PY_7P)(P(Y_4)(Y_5)(Y_6))_2Ir(BY)$ wherein BY is a boron moiety; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and
20 R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the
25 group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

In a further embodiment of the catalytic
30 composition, the iridium complex is $(P^{\sim}P)(P(Y_4)(Y_5)(Y_6))_2Ir(BY)$ wherein BY is a boron moiety; Y_4 , Y_5 , and Y_6 are each selected from the group

consisting of hydrogen, halide, alkyl, aryl, alkoxide
 (-O(R₁₁)), and amide (-N(R₁₂)(R₁₃)) wherein R₁₁, R₁₂, and
 R₁₃ are each selected from the group consisting of
 hydrogen, linear alkyl containing 1 to 8 carbon atoms,
 5 branched alkyl containing 1 to 8 carbons, and a carbon
 in a cyclic structure; and wherein (P~P) is of the
 formula

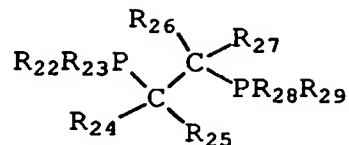


wherein R₂₂, R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈, and R₂₉ are each
 10 selected from the group consisting of alkyl chains,
 carbocyclic rings, and aryl groups.

In a further embodiment of the catalytic
 composition, the iridium complex is
 (PY₇P)(P(R₁₄)(R₁₅)(R₁₆))₂Ir(BY) wherein BY is a boron
 15 moiety; R₁₄, R₁₅, and R₁₆ are each selected from the
 group consisting of hydrogen, linear alkyl, branched
 alkyl, and a carbon in a cyclic structure; (PY₇P) is
 R₁₈R₁₉P-Y₇-PR₂₀R₂₁ wherein R₁₈, R₁₉, R₂₀, and R₂₁ are each
 selected from the group consisting of hydrogen, linear
 20 alkyl containing 1 to 8 carbon atoms, branched alkyl
 containing 1 to 8 carbons, and a carbon in a cyclic
 structure, and Y₇ is a chain containing 1 to 12
 carbons.

In a further embodiment of the catalytic
 25 composition, the iridium complex is
 (P~P)(P(R₁₄)(R₁₅)(R₁₆))₂Ir(BY) wherein BY is a boron
 moiety; R₁₄, R₁₅, and R₁₆ are each selected from the
 group consisting of hydrogen, linear alkyl, branched
 alkyl, and a carbon in a cyclic structure; and wherein

(P⁻P) is of the formula

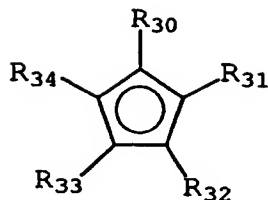


wherein R₂₂, R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈, and R₂₉ are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

In a further embodiment of the catalytic composition, the iridium complex is selected from the group consisting of (Cp*)Ir(H)₂(Me₃P), (Cp*)Ir(H)(BPin)(Me₃P), (Cp*)Ir(H)(C₆H₅)(Me₃P), (Ind)Ir(COD), (MesH)Ir(BPin)(B(OR)₂), ((R₁)₃P)₃Ir(B(OR)₂)₂, (R₁)₂P)₂Ir(BPin)₃, [((R₁)₂P)₃Ir((R₂O)₂B)₃]₂, ((R₁)₃P)₄Ir(BPin), ((R₁)₂P)₂Ir(BPin)₃, (MesH)Ir(BPin)₃, IrCl(COD), and [IrCl(COD)]₂, wherein CP* is 1,2,3,4,5-methylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, P is phosphorus, Ind is indenyl, COD is 1,5-cyclooctadiene, MesH is mesitylene, and wherein R, R₁, and R₂ are each selected from the group consisting of hydrogen, linear or branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure.

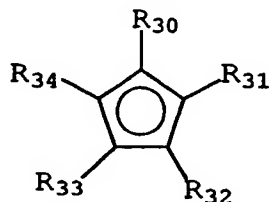
In a further embodiment of the catalytic composition, the rhodium complex is (Cp')(P(Y₄)(Y₅)(Y₆))Rh(H)_n(BY)_{2-n} wherein Y₄, Y₅, and Y₆ are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide (-O(R₁₁)), and amide (-N(R₁₂)(R₁₃)) wherein R₁₁, R₁₂, and R₁₃ are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic

structure; n is 0 or 1; BY is a boron moiety; and Cp' is of the formula



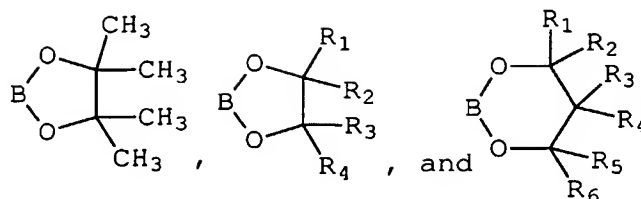
wherein R_{30} , R_{31} , R_{32} , R_{33} , and R_{34} are each selected from the group consisting of hydrogen, alkyl chains, carbocyclic rings, and aryl groups.

In a further embodiment of the catalytic composition, the rhodium complex is $(Cp')(P(R_{10}(R_{11})(R_{12})))Rh(H)_n(BY)_{2-n}$ wherein R_{10} , R_{11} , and R_{12} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; n is 0 or 1; BY is a boron moiety; and Cp' is of the formula



wherein R_{30} , R_{31} , R_{32} , R_{33} , and R_{34} are each selected from the group consisting of hydrogen, alkyl chains, carbocyclic rings, and aryl groups.

In a preferred embodiment of the above iridium and rhodium catalytic compositions, BY is selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

In a further embodiment of the catalytic composition, the rhodium complex is selected from the group consisting of $(Cp^*)Rh(H)_2(Me_3P)$, $(Cp^*)Rh(H)(BPin)(Me_3P)$, $(Cp^*)Rh(H)(C_6H_5)(Me_3P)$, and $(Cp^*)Rh(\text{hexamethylbenzene})$, wherein Cp^* is 1,2,3,4,5-methylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, and P is phosphorus.

The present invention provides a process for producing a ring-substituted arene borane which comprises reacting a ring-substituted arene with an HB organic compound in the presence of a catalytically effective amount of an iridium or rhodium complex with three or substituents, excluding hydrogen, bonded to the iridium or rhodium, to form the ring-substituted arene borane.

In a further embodiment, the present invention provides a process for producing a ring-substituted arene borane which comprises reacting a ring-substituted arene with an HB organic compound in the presence of a catalytically effective amount of an iridium or rhodium complex with three or substituents, excluding hydrogen, bonded to the iridium or rhodium

and a phosphorus organic ligand, in a molar ratio of complex to ligand between about 1 to 3 and 1 to 1, wherein the ligand is at least in part bonded to the iridium or rhodium, to form the ring-substituted arene borane.

Preferably, the phosphorus organic ligand is selected from the group consisting of trimethyl phosphine (PMe_3), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,2-bis(diphenylphosphino)ethane (dppe).

In a further embodiment of the process, the iridium complex is $(\text{ArH})\text{Ir}(\text{BY})_3$ wherein ArH is selected from the group consisting of aromatic, heteroaromatic, polyaromatic, and heteropolyaromatic hydrocarbon; and BY is a boron moiety.

In a further embodiment of the process, the iridium complex is $(\text{MesH})\text{Ir}(\text{BY})_3$ wherein MesH is mesitylene; and BY is a boron moiety.

In a further embodiment of the process, the iridium complex is $(\text{P}(\text{Y}_4)(\text{Y}_5)(\text{Y}_6))_3\text{Ir}(\text{H})_n(\text{BY})_{3-n}$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-\text{O}(\text{R}_{11})$), and amide ($-\text{N}(\text{R}_{12})(\text{R}_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; n is 0, 1, or 2; and BY is a boron moiety.

In a further embodiment of the process, the iridium complex is $(\text{P}(\text{R}_{14})(\text{R}_{15})(\text{R}_{16}))_3\text{Ir}(\text{H})_n(\text{BY})_{3-n}$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; n is 0, 1,

or 2; and BY is a boron moiety.

In a further embodiment of the process, the iridium complex is $(P(Y_4)(Y_5)(Y_6))_3Ir(H)(R_{17})(BY)$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; R_{17} is selected from the group consisting of a linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure; and BY is a boron moiety.

In a further embodiment of the process, the iridium complex is $(P(R_{14})(R_{15})(R_{16}))_3Ir(H)(R_{17})(BY)$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; R_{17} is selected from the group consisting of a linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure; and BY is a boron moiety.

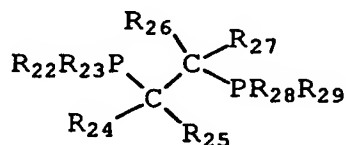
In a further embodiment of the process, the iridium complex is $\{(PY_7P)Ir(BY)_3\}_2(\mu_2-(PY_7P))$ wherein BY is a boron moiety; (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

In a further embodiment of the process, the

iridium complex is $(PY_7P)(P(Y_4)(Y_5)(Y_6))Ir(BY)_3$ wherein BY is a boron moiety; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide $(-O(R_{11}))$, and amide $(-N(R_{12})(R_{13}))$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

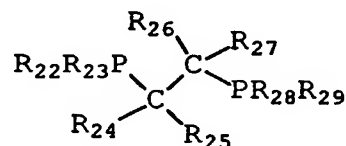
In a further embodiment of the process, the iridium complex is $(PY_7P)(P(R_{14})(R_{15})(R_{16}))Ir(BY)_3$ wherein BY is a boron moiety; R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

In a further embodiment of the process, the iridium complex is $\{(P^{\wedge}P)Ir(BY)_3\}_2(\mu_2-(P^{\wedge}P))$ wherein BY is a boron moiety and wherein $(P^{\wedge}P)$ is of the formula



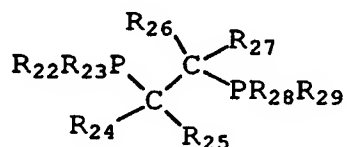
wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

In a further embodiment of the process, the
 5 iridium complex is $(P^{\sim}P)(P(Y_4)(Y_5)(Y_6))Ir(BY)_3$ wherein
 BY is a boron moiety; Y_4 , Y_5 , and Y_6 are each selected
 from the group consisting of hydrogen, halide, alkyl,
 aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$)
 wherein R_{11} , R_{12} , and R_{13} are each selected from the
 10 group consisting of hydrogen, linear alkyl containing
 1 to 8 carbon atoms, branched alkyl containing 1 to 8
 carbons, and a carbon in a cyclic structure; and
 wherein $(P^{\sim}P)$ is of the formula



15 wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each
 selected from the group consisting of alkyl chains,
 carbocyclic rings, and aryl groups.

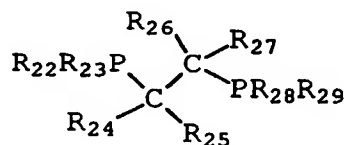
In a further embodiment of the process, the
 iridium complex is $(P^{\sim}P)(P(R_{14})(R_{15})(R_{16}))Ir(BY)_3$ wherein
 20 BY is a boron moiety; R_{14} , R_{15} , and R_{16} are each
 selected from the group consisting of hydrogen, linear
 alkyl, branched alkyl, and a carbon in a cyclic
 structure; and wherein $(P^{\sim}P)$ is of the formula



25 wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each
 selected from the group consisting of alkyl chains,
 carbocyclic rings, and aryl groups.

In a further embodiment of the process, the iridium complex is $(PY_7P)Ir(BY)_3$ wherein BY is a boron moiety; and (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

In a further embodiment of the process, the iridium complex is $(P^{\wedge}P)Ir(BY)_3$ wherein BY is a boron moiety and wherein $(P^{\wedge}P)$ is of the formula



wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

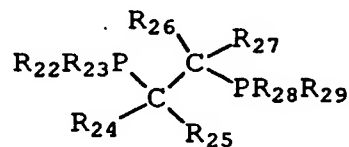
In a further embodiment of the process, the iridium complex is $(P(Y_4)(Y_5)(Y_6))_4Ir(BY)$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide $(-O(R_{11}))$, and amide $(-N(R_{12})(R_{13}))$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and BY is a boron moiety.

In a further embodiment of the process, the iridium complex is $(P(R_{14})(R_{15})(R_{16}))_4Ir(BY)$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; and BY is a boron

moiety.

In a further embodiment of the process, the iridium complex is $(PY_7P)(P(Y_4)(Y_5)(Y_6))_2Ir(BY)$ wherein BY is a boron moiety; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide $(-O(R_{11}))$, and amide $(-N(R_{12})(R_{13}))$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

In a further embodiment of the process, the iridium complex is $(P^{\sim}P)(P(Y_4)(Y_5)(Y_6))_2Ir(BY)$ wherein BY is a boron moiety; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide $(-O(R_{11}))$, and amide $(-N(R_{12})(R_{13}))$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and wherein $(P^{\sim}P)$ is of the formula

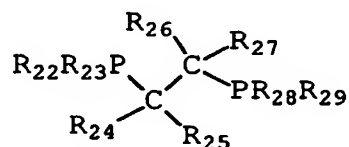


wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains,

carbocyclic rings, and aryl groups.

In a further embodiment of the process, the iridium complex is $(PY_7P)(P(R_{14})(R_{15})(R_{16}))_2Ir(BY)$ wherein BY is a boron moiety; R_{14} , R_{15} , and R_{16} are each
 5 selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon
 10 atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

In a further embodiment of the process, the iridium complex is $(P^{\sim}P)(P(R_{14})(R_{15})(R_{16}))_2Ir(BY)$ wherein
 15 BY is a boron moiety; R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; and wherein $(P^{\sim}P)$ is of the formula

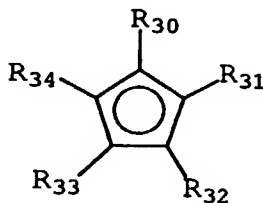


20 wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

In a further embodiment of the process, the iridium complex is selected from the group consisting
 25 of $(Cp^*)Ir(H)_2(Me_3P)$, $(Cp^*)Ir(H)(BPin)(Me_3P)$,
 $(Cp^*)Ir(H)(C_6H_5)(Me_3P)$, $(Ind)Ir(COD)$,
 $(MesH)Ir(BPin)(B(OR)_2)$, $((R_1)_3P)_3Ir(B(OR)_2)_3$,
 $(R_1)_2P)_2Ir(BPin)_3$, $[((R_1)_2P)_3Ir((R_2O)_2B)_3]_2$,
 $((R_1)_3P)_4Ir(BPin)$, $((R_1)_2P)_2Ir(BPin)_3$, $(MesH)Ir(BPin)_3$,

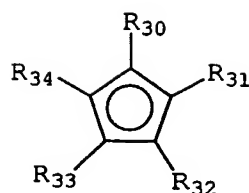
IrCl(COD), and $[\text{IrCl}(\text{COD})]_2$, wherein CP^* is 1,2,3,4,5-methylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, P is phosphorus, Ind is indenyl, COD is 1,5-cyclooctadiene, MesH is
 5 mesitylene, and wherein R, R_1 , and R_2 are each selected from the group consisting of hydrogen, linear or branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure.

In a further embodiment of the process, the
 10 rhodium complex is $(\text{Cp}')(\text{P}(\text{Y}_4)(\text{Y}_5)(\text{Y}_6))\text{Rh}(\text{H})_n(\text{BY})_{2-n}$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-\text{O}(\text{R}_7)$), and amide ($-\text{N}(\text{R}_8)(\text{R}_9)$) wherein R_7 , R_8 , and R_9 are each selected from the group consisting of
 15 hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; n is 0 or 1; BY is a boron moiety; and Cp' is of the formula



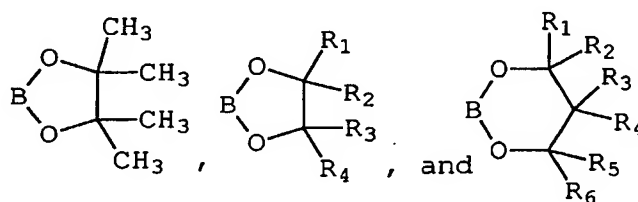
20 wherein R_{30} , R_{31} , R_{32} , R_{33} , and R_{34} are each selected from the group consisting of hydrogen, alkyl chains, carbocyclic rings, and aryl groups.

In a further embodiment of the process, the
 rhodium complex is $(\text{Cp}')(\text{P}(\text{R}_{10}(\text{R}_{11})(\text{R}_{12})))\text{Rh}(\text{H})_n(\text{BY})_{2-n}$
 25 wherein R_{10} , R_{11} , and R_{12} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; n is 0 or 1; BY is a boron moiety; and Cp' is of the formula



wherein R_{30} , R_{31} , R_{32} , R_{33} , and R_{34} are each selected from the group consisting of hydrogen, alkyl chains, carbocyclic rings, and aryl groups.

5 In a preferred embodiment of the process, BY is selected from the group consisting of

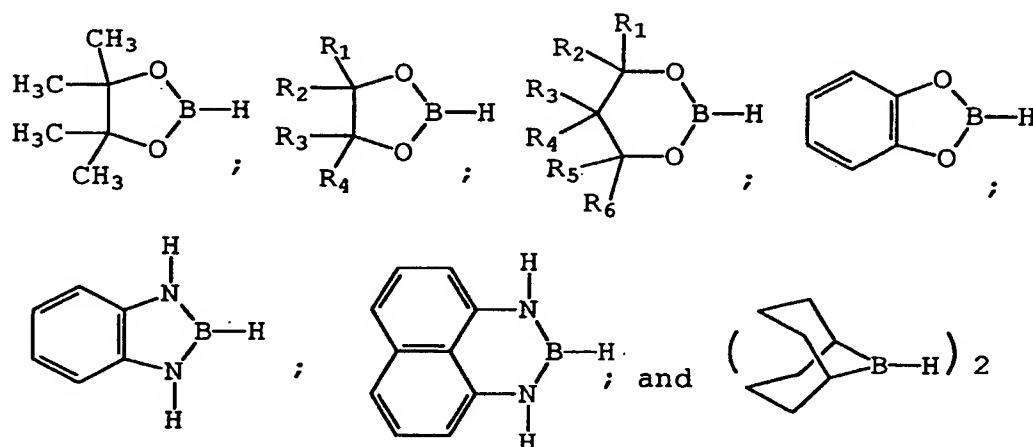


10 wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

15 In a further embodiment of the process, the rhodium complex is selected from the group consisting of $(Cp^*)Rh(H)_2(Me_3P)$, $(Cp^*)Rh(H)(BPin)(Me_3P)$, $(Cp^*)Rh(H)(C_6H_5)(Me_3P)$, and $(Cp^*)Rh(\text{hexamethylbenzene})$, wherein Cp^* is 1,2,3,4,5-methylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, and P is phosphorus.

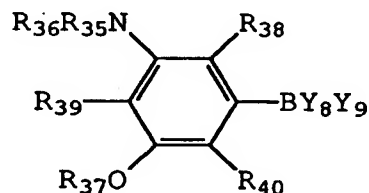
20 In a further embodiment of the process, the HB organic ligand is selected from the group consisting of $B(H)(Y_{11})(Y_{12})$ wherein Y_{11} and Y_{12} are each selected from the group consisting of hydrogen,

halide, alkyl, aryl, alkoxide ($-\text{O}(\text{R}_7)$), and amide ($-\text{N}(\text{R}_8)(\text{R}_9)$) wherein R_7 , R_8 , and R_9 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; (B(H) ($\text{Y}_{13}-\text{Y}_{14}-\text{Y}_{15}$) wherein Y_{13} and Y_{15} are each selected from the group consisting of alkyl, aryl, oxygen, and nitrogen and Y_{14} is a chain containing 1 to 12 carbon atoms;



10

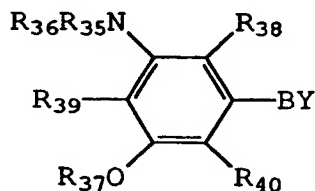
The present invention further provides a ring-substituted arene borane of the formula



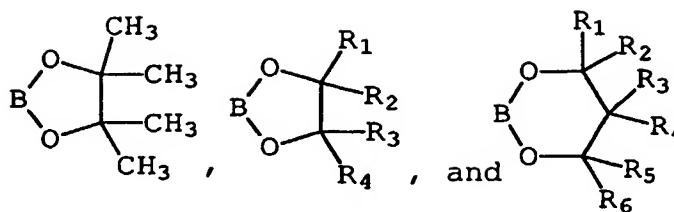
wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron; R_{35} , R_{36} , and R_{37} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms,

branched alkyl containing 1 to 8 carbon atoms, aryl,
carbon within a cyclic structure, a silicon containing
moiety wherein the silicon is bound to a nitrogen or
oxygen which is bound to the aromatic ring, amine
5 protecting group, and alcohol protecting group; and
 R_{38} , R_{39} , and R_{40} are each selected from the group
consisting of hydrogen, halide, alkyl, aryl, alkoxide,
amide, and a group containing any other element which
is bound to the aromatic ring.

10 The present invention further provides a
ring-substituted arene borane of the formula

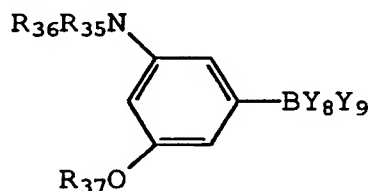


wherein R_{35} , R_{36} , and R_{37} are each selected from the
group consisting of hydrogen, linear alkyl containing
15 1 to 8 carbon atoms, branched alkyl containing 1 to 8
carbon atoms, aryl, carbon within a cyclic structure,
a silicon containing moiety wherein the silicon is
bound to a nitrogen or oxygen which is bound to the
aromatic ring, amine protecting group, and alcohol
20 protecting group; and R_{38} , R_{39} , and R_{40} are each
selected from the group consisting of hydrogen,
halide, alkyl, aryl, alkoxide, amide, and a group
containing any other element which is bound to the
aromatic ring; and BY is a boron moiety selected from
25 the group consisting of



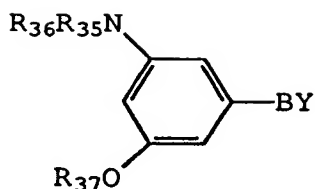
wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, and carbon within a cyclic structure.

The present invention further provides a ring-substituted arene borane of the formula

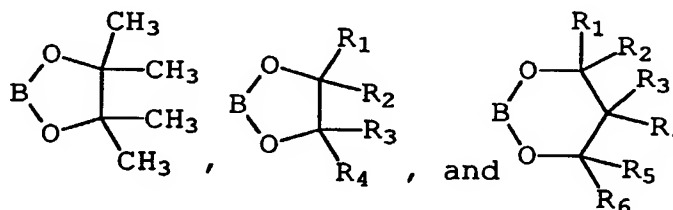


wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron; and R_{35} , R_{36} , and R_{37} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group.

The present invention further provides a ring-substituted arene borane of the formula

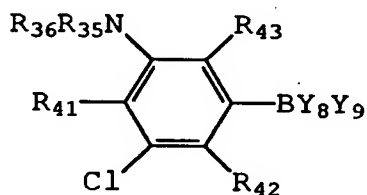


wherein R_{35} , R_{36} , and R_{37} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, and carbon within a cyclic structure.

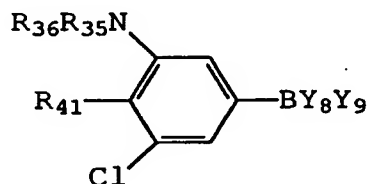
The present invention further provides a ring-substituted arene borane of the formula



wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide,

amide, and a group containing any other element wherein the element is bound to boron; R_{35} and R_{36} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched
 5 alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and R_{41} , R_{42} , and
 10 R_{43} are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element which is bound to the aromatic ring.

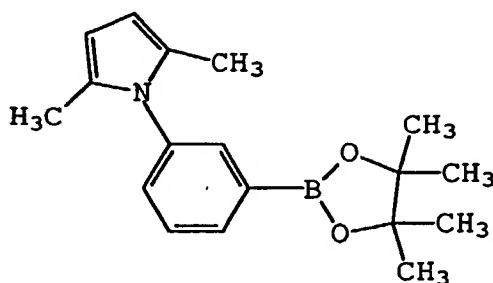
The present invention further provides a
 15 ring-substituted arene borane of the formula



wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element
 20 wherein the element is bound to boron; R_{35} and R_{36} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety
 25 wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and R_{41} is selected from the group consisting of halide, alkyl, aryl, alkoxide, amide, and a group containing any

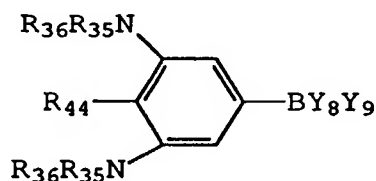
other element except hydrogen which is bound to the aromatic ring.

The present invention further provides a ring-substituted arene borane of the formula



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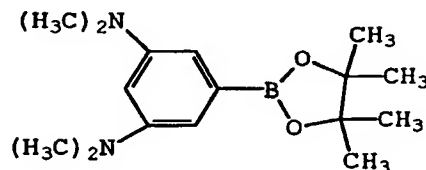
The present invention further provides a ring-substituted arene borane of the formula



- 10 wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron; R_{35} and R_{36} are each selected from the group consisting of hydrogen,
- 15 linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting
- 20 group, and alcohol protecting group; and R_{44} is selected from the group consisting of alkoxide, amide, and a group containing any other element which is bound to the aromatic ring except for hydrogen or

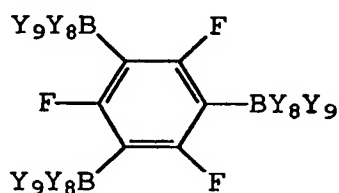
carbon.

The present invention further provides a ring-substituted arene borane of the formula



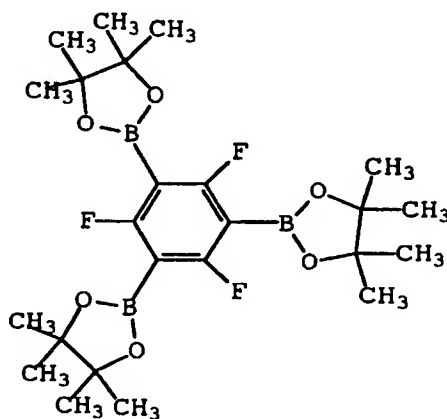
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The present invention further provides a ring-substituted arene borane of the formula



wherein Y_8 and Y_9 are each selected from the group
 10 consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron.

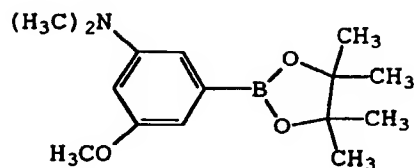
The present invention further provides a ring-substituted arene borane of the formula



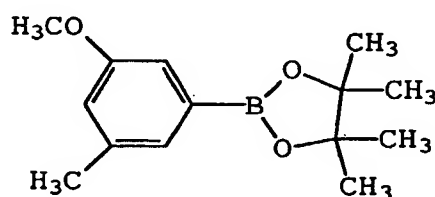
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The present invention further provides a

ring-substituted arene borane of the formula



The present invention further provides a
5 ring-substituted arene borane of the formula



OBJECTS

10 It is an object of the present invention to provide a general process for synthesizing boronic esters and acids which avoids many of the limitations of the prior art processes.

A further object of the present invention is
15 to provide a general process for synthesizing boronic esters and acids by metal catalyzed activations of C-H bonds in hydrocarbon feedstocks and B-H bonds in boron reagents to produce novel B-C bonds with hydrogen as the sole byproduct of the process.

20 A further still object of the present invention is to provide catalysts which can be used for the general process for synthesizing boronic esters and acids.

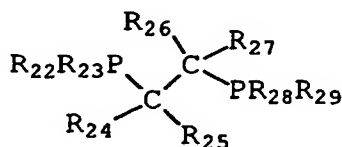
These and other objects of the present
25 invention will become increasingly apparent with

reference to the following drawings and preferred embodiments.

DETAILED DESCRIPTION OF THE DRAWINGS

5 Figure 1 shows the formulas for precatalysts 1 to 15. CP* is 1,2,3,4,5-methylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, P is phosphorus, Ind is indenyl, COD is 1,5-cyclooctadiene, MesH is mesitylene, and wherein R, R₁,
10 and R₂ are each selected from the group consisting of hydrogen, linear or branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure.

 Figure 2 shows the formulas for precatalysts 16 to 27. Y₄, Y₅, and Y₆ are each selected from the
15 group consisting of hydrogen, halide, alkyl, aryl, alkoxide (-O(R₁₁)), and amide (-N(R₁₂)(R₁₃)) wherein R₁₁, R₁₂, and R₁₃ are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a
20 carbon in a cyclic structure; R₁₄, R₁₅, and R₁₆ are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; (PY₇P) is R₁₈R₁₉P-Y₇-PR₂₀R₂₁ wherein R₁₈, R₁₉, R₂₀, and R₂₁ are each selected from the group consisting
25 of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y₇ is a chain containing 1 to 12 carbons; (P~P) is of the formula



wherein R₂₂, R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈, and R₂₉ are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups; and BY is a boron moiety.

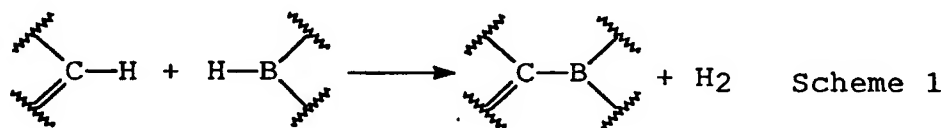
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DETAILED DESCRIPTION OF THE INVENTION

All patents, patent applications, provisional patent applications, government publications, government regulations, and literature references cited in this specification are hereby incorporated herein by reference in their entirety. In case of conflict, the present description, including definitions, will control.

The present invention provides catalysts comprising iridium (Ir) or rhodium (Rh) in a complex with three or more substituents, excluding hydrogen, bonded to the Ir or Rh and a phosphorus organic ligand, which is at least in part bonded to the Ir or Rh and processes for forming B-C bonds between boranes and sp²-hybridized C-H bonds to produce organoboron complexes such as ring-substituted arenes (or aryl boronate esters and acids) according to the process shown in Scheme 1.

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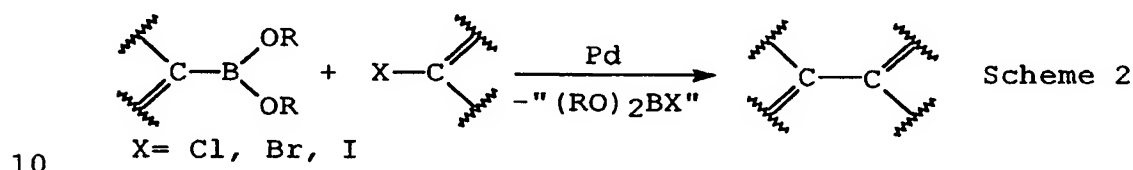


25

The direct route to aryl boronate esters and acids using the catalysts and process of the present invention is particularly useful for producing ring-substituted arene boranes (aryl boronic esters and acids) which are versatile transfer reagents in

30

organic chemistry. The boron in these transfer reagents serves as a mask for a broad range of heteroatoms and functional groups. Some of the most remarkable and broadly used applications of organoboron chemistry are catalytic cross-coupling reactions of C-B and C-X (X is Cl, Br, I) groups which yield new C-C bonds as shown in scheme 2. In addition, the present invention provides novel boranes and novel organoborane complexes.



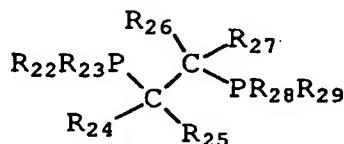
The novel boranes and organoborane complexes are particularly useful in the pharmaceutical industry as key building blocks for drug manufacturing and as versatile reagents for high-throughput parallel synthesis in drug discovery. In addition, the borane and organoboron complexes are useful for the manufacture of chemical sensing and high-performance specialty polymers.

20 The B-C bond-forming reactions between boranes and sp²-hybridized C-H bonds are catalyzed by the catalysts of the present invention which comprise Ir and Rh in a complex with three or more substituents, excluding hydrogen, bonded to the Ir or Rh and a phosphorus organic ligand, which is at least in part bonded to the Ir or Rh. Preferably, the catalysts comprise iridium or rhodium in a complex with three or more substituents, excluding hydrogen, bonded to the iridium or rhodium and an organic ligand

selected from the group consisting of a phosphorus organic ligand, an organic amine, an imine, a nitrogen heterocycle, and an ether in a molar ratio between about 1 to 3 and 1 to 1, wherein the ligand is at least in part bonded to the iridium or rhodium. Effective precatalysts can be grouped into two families: those that contain cyclopentadienyl (Cp^* , C_5R_5 wherein R is CH_3) or indenyl (Ind, C_9R_7 wherein R is H) ligands and those that contain phosphine ligands. Included are compounds that contain both the Cp^* and the Ind ligands and the phosphine ligands.

Preferably, the catalytic composition comprising iridium comprises one of the following: $(ArH)Ir(BY)_3$ wherein ArH is selected from the group consisting of aromatic, heteroaromatic, polyaromatic, and heteropolyaromatic hydrocarbon and wherein BY is a boron moiety; $(MesH)Ir(BY)_3$ wherein MesH is mesitylene and wherein BY is a boron moiety; $(P(Y_4)(Y_5)(Y_6))_3Ir(H)_n(BY)_{3-n}$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, wherein n is 0, 1, or 2, and wherein BY is a boron moiety; $(P(R_{14})(R_{15})(R_{16}))_3Ir(H)_n(BY)_{3-n}$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure, wherein n is 0, 1, or 2, and wherein BY is a boron moiety; $(P(Y_4)(Y_5)(Y_6))_3Ir(H)(R_{13})(BY)$ wherein Y_4 , Y_5 , and Y_6 are as above, wherein R_{13} is selected from the

group consisting of a linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure, and wherein BY is a boron moiety; $(P(R_{14})(R_{15})(R_{16}))_3Ir$
 5 $(H)(R_{17})(BY)$ wherein R_{14} , R_{15} , and R_{16} are as above; R_{17} is as above, and wherein BY is a boron moiety;
 $\{(PY_7P)Ir(BY)_3\}_2(\mu_2-(PY_7P))$ (16) wherein BY is a boron moiety, wherein (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group
 10 consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and wherein Y_7 is a chain containing 1 to 12 carbons;
 $(PY_7P)(P(Y_4)(Y_5)(Y_6))Ir(BY)_3$ (17) wherein BY is a boron
 15 moiety, wherein Y_4 , Y_5 , and Y_6 are as above, and wherein (PY_7P) is as above;
 $(PY_7P)(P(R_{10})(R_{11})(R_{12}))Ir(BY)_3$ (18) wherein BY is a boron moiety, wherein R_{14} , R_{15} , and R_{16} are as above, wherein (PY_7P) is as above; $\{(P^{\wedge}P)Ir(BY)_3\}_2(\mu_2-(P^{\wedge}P))$
 20 (19) wherein BY is a boron moiety and wherein $(P^{\wedge}P)$ is of the formula



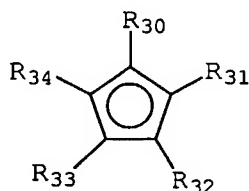
wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups;
 25 $(P^{\wedge}P)(P(Y_4)(Y_5)(Y_6))Ir(BY)_3$ (20) wherein BY is a boron moiety, wherein Y_4 , Y_5 , and Y_6 are as above, and wherein $(P^{\wedge}P)$ is as above; $(P^{\wedge}P)(P(R_{14})(R_{15})(R_{16}))Ir(BY)_3$
 (21) wherein BY is a boron moiety, wherein R_{14} , R_{15} , and

R_{16} are as above, and wherein $(P^{\wedge}P)$ is as above;
 $(PY_7P)Ir(BY)_3$ (22) wherein BY is a boron moiety, and
 wherein (PY_7P) is as above; $(P^{\wedge}P)Ir(BY)_3$ (23)
 wherein BY is a boron moiety, and wherein $(P^{\wedge}P)$ is as
 5 above; $(P(Y_4)(Y_5)(Y_6))_4Ir(BY)$ wherein Y_4 , Y_5 , and Y_6 are
 as above and BY is a boron moiety;
 $(P(R_{14})(R_{15})(R_{16}))_4Ir(BY)$ wherein R_{14} , R_{15} , and R_{16} are as
 above and BY is a boron moiety;
 $(PY_7P)(P(Y_4)(Y_5)(Y_6))_2Ir(BY)$ (24) wherein BY is a boron
 10 moiety, wherein Y_4 , Y_5 , and Y_6 are above, and wherein
 (PY_7P) is as above; $(P^{\wedge}P)(P(Y_4)(Y_5)(Y_6))_2Ir(BY)$ (25)
 wherein BY is a boron moiety, wherein Y_4 , Y_5 , and Y_6
 are as above, and wherein $(P^{\wedge}P)$ is as above;
 $(PY_7P)(P(R_{14})(R_{15})(R_{16}))_2Ir(BY)$ (26) wherein BY is a
 15 boron moiety, R_{14} , R_{15} , and R_{17} are as above, and
 wherein (PY_7P) is as above;
 $(P^{\wedge}P)(P(R_{14})(R_{15})(R_{16}))_2Ir(BY)$ (27) wherein BY is a boron
 moiety, wherein R_{14} , R_{15} , and R_{16} are as above, and
 wherein $(P^{\wedge}P)$ is as above.

20 Examples of catalytic compositions
 comprising iridium include those selected from the
 group consisting of $(Cp^*)Ir(H)_2(Me_3P)$ (1),
 $(Cp^*)Ir(H)(BPin)(Me_3P)$ (2), $(Cp^*)Ir(H)(C_6H_5)(Me_3P)$ (3),
 $(Ind)Ir(COD)$ (8), $(MesH)Ir(BPin)(B(OR)_2)$ (9),
 25 $((R_1)_3P)_3Ir(B(OR)_2)_3$ (10), $(R_1)_2P)_2Ir(BPin)_3$ (11),
 $[((R_1)_2P)_3Ir((R_2O)_2B)_3]_2$ (12), $((R_1)_3P)_4Ir(BPin)$ (13),
 $((R_1)_2P)_2Ir(BPin)_3$ (14), $(MesH)Ir(BPin)_3$ (9 wherein
 $B(OR)_2$ is $BPin$), $IrCl(COD)$ (15) and $[IrCl(COD)]_2$,
 wherein Cp^* is 1,2,3,4,5-methylcyclopentadienyl, $BPin$
 30 is pinacolborane, Me is methyl, H is hydrogen, P is
 phosphorus, Ind is indenyl, COD is 1,5-cyclooctadiene,
 $MesH$ is mesitylene, and wherein R , R_1 , and R_2 are each

selected from the group consisting of hydrogen, linear or branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure.

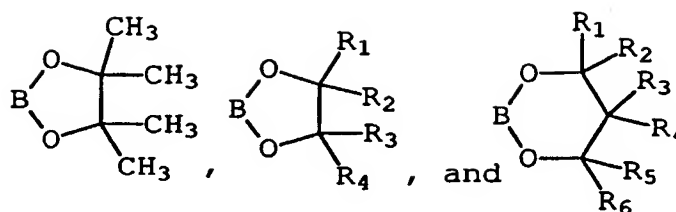
Preferably, the catalytic composition comprising rhodium comprises one of the following:
 $(Cp')(P(Y_4)(Y_5)(Y_6))Rh(H)_n(BY)_{2-n}$ wherein Y_4 , Y_5 , and Y_6 are as above, wherein n is 0 or 1, wherein BY is a boron moiety, and wherein Cp' is of the formula



wherein R_{30} , R_{31} , R_{32} , R_{33} , and R_{34} are each selected from the group consisting of hydrogen, alkyl chains, carbocyclic rings, and aryl groups; and
 $(Cp')(P(R_{14})(R_{15})(R_{16}))Rh(H)_n(BY)_{2-n}$ wherein R_{14} , R_{15} , and R_{16} are as above; n is 0 or 1, wherein BY is a boron moiety; and wherein Cp' is as above.

Examples of catalytic compositions comprising rhodium include those selected from the group consisting of $(Cp^*)Rh(H)_2(Me_3P)$ (4), $(Cp^*)Rh(H)(BPin)(Me_3P)$ (5), $(Cp^*)Rh(H)(C_6H_5)(Me_3P)$ (6), and $(Cp^*)Rh(\text{hexamethylbenzene})$ (7), wherein Cp^* is 1,2,3,4,5-methylcyclopentadienyl, $BPin$ is pinacolborane, Me is methyl, H is hydrogen, and P is phosphorus.

In the above catalytic compositions, preferably the BY boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure. Figures 1 and 2 show the structures of precatalysts 1 to 15 and 16 to 27, respectively.

While the precatalysts can under particular reaction conditions catalyze the borylation of particular ring-substituted arenes, the reactions proceed more efficiently when an organic ligand such as phosphine ligands (phosphorus organic ligands) are included in the reaction mixture. The addition of phosphine ligands to the reaction generates active catalysts which can produce ring-substituted arene borones (aryl boronate esters and acids) with low catalyst loading. The fact that phosphine-containing species can catalyze borylation is important because numerous phosphines are commercially available. Furthermore, the selectivities of the borylation can be altered as a function of the phosphine ligand that is added. Examples of phosphine ligands include, but are not limited to, trimethyl phosphine (PMe_3), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,2-bis(diphenylphosphino)ethane (dppe).

For example, precatalyst 8 can be obtained in two high-yielding steps from the common iridium starting material, $\text{IrCl}_3(\text{H}_2\text{O})_x$. Precatalyst 9 can be

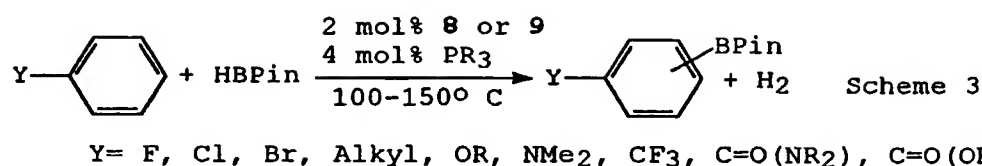
prepared by reacting 8 with approximately 5 equivalents of pinacolborane (HBPin) in mesitylene solvent. It was discovered that commercially available precatalyst 15 will also catalyze borylations. While all of the precatalysts have similar activities for many substrates, borylations of particular arenes exhibit a remarkable precatalyst dependence.

In the absence of phosphine ligands, compound 8 catalyzes the borylation of benzene by HBPin, but relatively high catalyst loading and long reaction times are required to prepare PhBPin in reasonable yields. At temperatures above 80° C, decomposition to Ir metal occurs, which halts catalysis. Compound 9 is not effective in catalysis without the addition of phosphine.

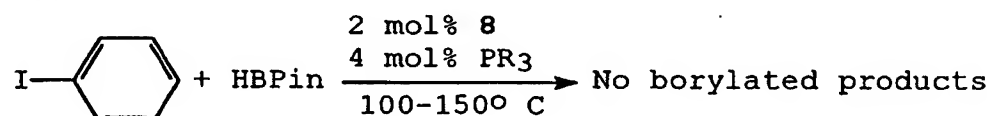
Addition of phosphine ligands to solutions of compound 8 and 9 generates active catalysts for the production of aryl boronic esters with low catalyst loading as illustrated for the examples in Figure 1. The fact that phosphine-containing species can catalyze borylation is important because numerous phosphines are commercially available. Consequently, the selectivities can be altered as a function of the phosphine that is added.

Another virtue of the present invention is that a broad range of heteroatoms and functional groups are inert under borylation conditions as shown in Scheme 3.

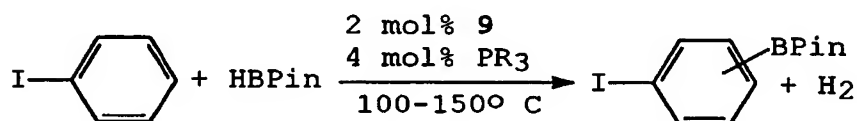
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Given that Grignard reagents react with several of these groups and Pd catalyzes the formation of ArBPin from ArBr and HBPin, the functional group tolerance for the Ir-catalyzed chemistry is remarkable. Under appropriate conditions, even iodobenzene can be borylated without iodide reduction. In this instance, no conversion was observed when using precatalyst 8, whereas precatalyst 9 gives the borylated products in 95% yield as shown in Scheme 4.

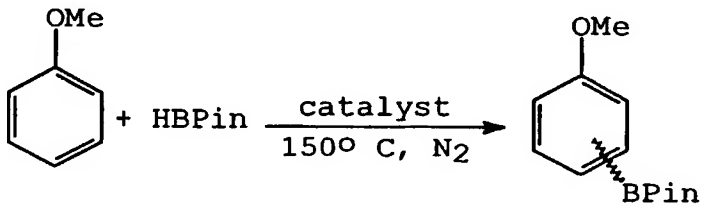


Scheme 4



Therefore, the present substrate compatibility, which is already remarkably broad, is expected to expand with further improvements to the present invention.

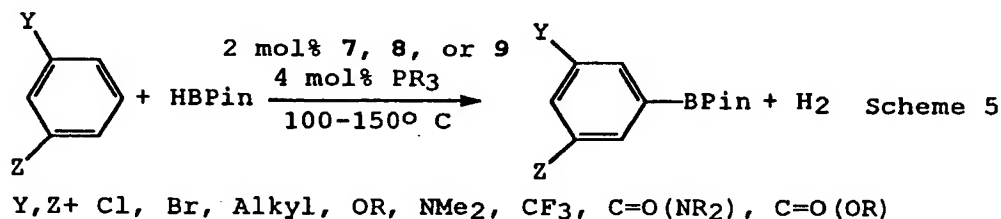
For monosubstituted arenes, mixtures of *meta* and *para* borylated products are obtained. In contrast to the known Rh complexes that catalyze aromatic borylation, the *meta:para* ratio deviates significantly from 2:1. For most substrates, this ratio exceeds 3:1 and data for anisole are shown in Table 1.

Table 1.				
Isomer distributions for catalytic borylations of anisole				
				
Entry	Catalyst	Temp (°C)	Time (h)	o:m:p
1	2 mol% 8/2 PMe ₃	150	29	9:74:17
2	2 mol% 9/2 PMe ₃	150	41	8:75:17
3	2 mol% 8/dppe	150	22	3:76:21
4	2 mol% 9/dppe	150	51	3:78:20
5	2 mol% 8/dppe	100	22	2:80:18
6	2 mol% 3/dppe	100	18	2:80:18
7	2 mol% 9	150	3	12:53:36 ^a
8	2 mol% 8/PMe ₃	150	29	2:57:40
9	2 mol% 9/PMe ₃	150	40	3:67:30
^a Low conversion. <i>o</i> is ortho, <i>m</i> is meta, and <i>p</i> is para. Dppe is 1,2-bis(diphenylphosphino)ethane				

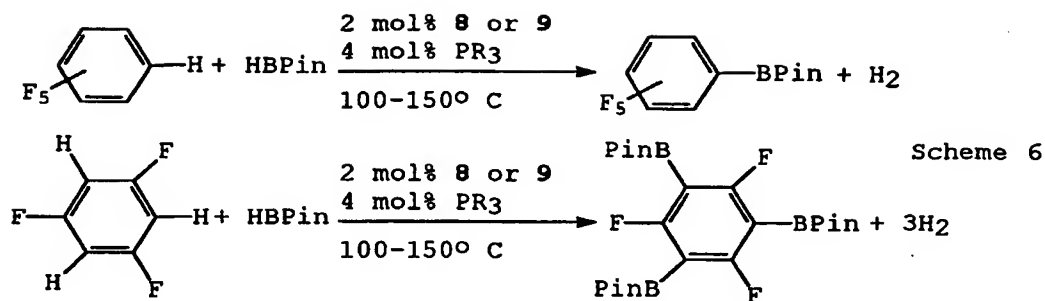
It is noteworthy that the para isomer is more favored for entries 7 and 8, where the *meta:para* ratio is significantly less than 2:1. These data show that while there is a steric bias against ortho borylation, the *meta:para* ratio is sensitive to the type and amount of phosphine ligands that are added. For dppe, the activity at 100° C is relatively high, and the reaction is complete in less time than at 150° C.

With the exception of F, and amide functional groups in some Rh catalyzed reactions, borylation at positions that are ortho to functional groups are avoided. Thus, 1,3-substituted aromatics can be selectively borylated at the 5' position. This is the hardest position to selectively activate by traditional aromatic substitution chemistry and for electron rich arenes, there are no general methods for preparing derivatives from the 1,3-substituted arenes.

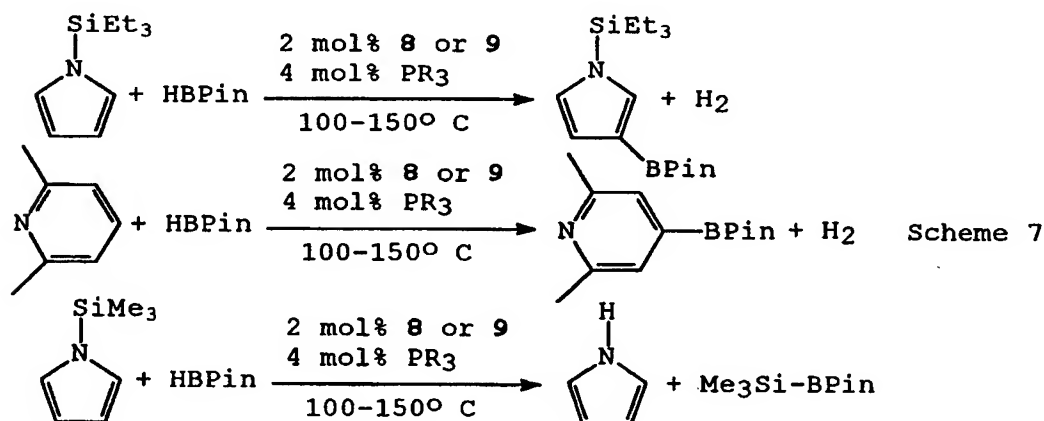
Furthermore, multiple borylation of 1,3-substituted arenes does not occur to a significant extent, which means that equimolar quantities of borane and arene give aromatic boronic esters in high yield in the absence of solvent. Substrates that have been successfully converted to boronate esters under these conditions are shown in scheme 5.



For fluorinated benzenes, the borylation at ortho positions occurs readily. Hence, C₆H₅F and 1,3,5-trifluorobenzene give mono and triborylated products, respectively, as shown in Scheme 6.



It is noteworthy that present Rh catalysts are not compatible with halide functionalities and substantial quantities of dehalogenated and diborylated products are observed. We extended the chemistry to five-membered rings and heterocycles as shown by the borylation of a protected pyrrole and 2,6-lutidine in Scheme 7

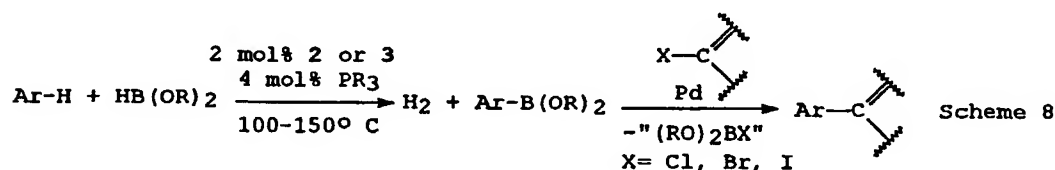


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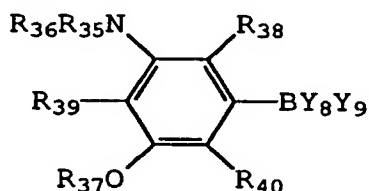
Interestingly, it was found that $(\text{CH}_3)_3\text{Si-BPiBn}$ is produced catalytically when the C-H activation of N-trimethylsilyl pyrrole was attempted. Since Si-B reagents interesting chemistry, this provides a very simple route as compared to most of the known methods.

Lastly, we have demonstrated that aromatic borylation of one aromatic substrate and subsequent

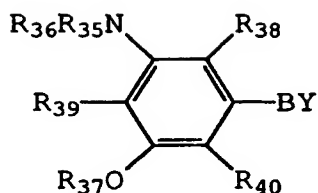
coupling with a second sp^2 -hybridized halocarbon can be achieved in one pot as shown in Scheme 8. One extension of this concept is the development of a catalyst kit that can be used for general couplings in drug discovery applications.



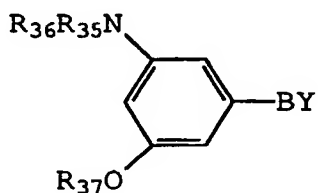
The following ring-substituted arene boranes have been synthesized according to the process of the present invention:



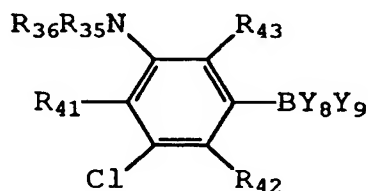
wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron; R_{35} , R_{36} , and R_{37} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and R_{38} , R_{39} , and R_{40} are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element which is bound to the aromatic ring;



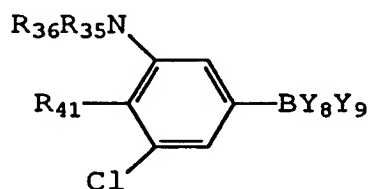
wherein R_{35} , R_{36} , and R_{37} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and R_{38} , R_{39} , and R_{40} are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element which is bound to the aromatic ring; and wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron; and R_{35} , R_{36} , and R_{37} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group;



wherein R_{35} , R_{36} , and R_{37} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure,
 5 a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and BY is a boron moiety;

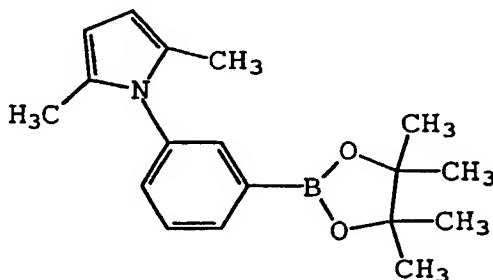


10 wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron; R_{35} and R_{36} are each selected from the group consisting of hydrogen,
 15 linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting
 20 group, and alcohol protecting group; and R_{41} , R_{42} , and R_{43} are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element which is bound to the aromatic ring;

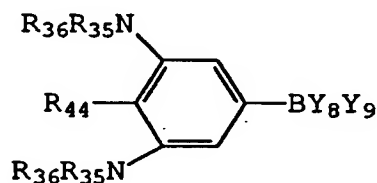


25

wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron; R_{35} and R_{36} are
 5 each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen
 10 which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and R_{41} is selected from the group consisting of halide, alkyl, aryl, alkoxide, amide, and a group containing any other element except hydrogen which is bound to the
 15 aromatic ring;

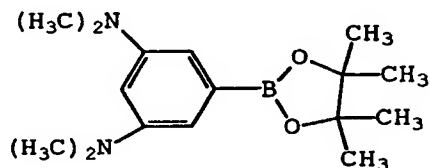


;

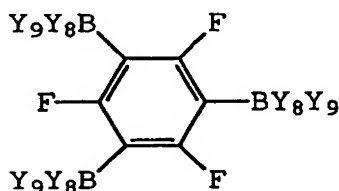


wherein Y_8 and Y_9 are each selected from the group
 20 consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron; R_{35} and R_{36} are each selected from the group consisting of hydrogen,

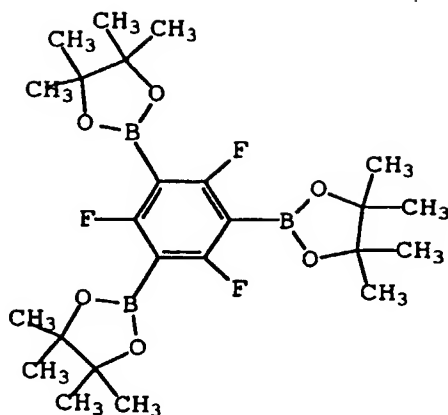
linear alkyl containing 1 to 8 carbon atoms, branched
 alkyl containing 1 to 8 carbon atoms, aryl, carbon
 within a cyclic structure, a silicon containing moiety
 wherein the silicon is bound to a nitrogen or oxygen
 5 which is bound to the aromatic ring, amine protecting
 group, and alcohol protecting group; and R_{44} is
 selected from the group consisting of alkoxide, amide,
 and a group containing any other element which is
 bound to the aromatic ring except for hydrogen or
 10 carbon;



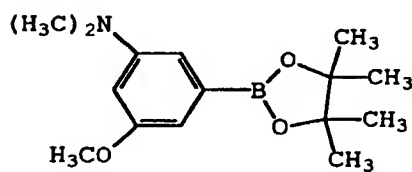
;



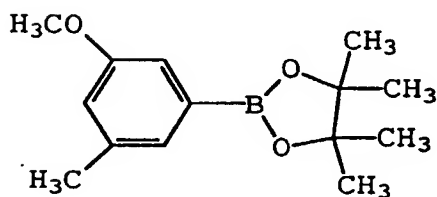
wherein Y_8 and Y_9 are each selected from the group
 15 consisting of hydrogen, halide, alkyl, aryl, alkoxide,
 amide, and a group containing any other element
 wherein the element is bound to boron;



;

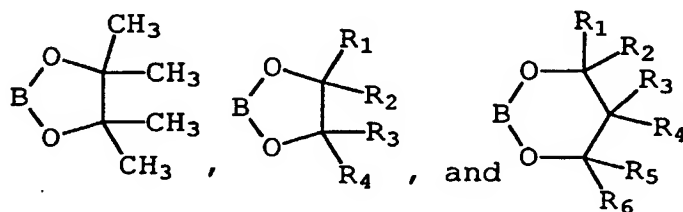


; and,



5

In the above ring-substituted arene boranes, BY is a boron moiety selected from the group consisting of



10

wherein R₁, R₂, R₃, R₄, R₅, and R₆ are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl

containing 1 to 8 carbon atoms, aryl, and carbon within a cyclic structure.

The process and catalysts of the present invention for making ring-substituted arene boranes (aryl boronate esters and acids) avoid many of the limitations of the prior art because (1) the reactions can be carried out in neat substrates, thereby avoiding ethereal solvents, (2) since the C-H bonds are selectively activated, halogenation of arenes and conversions to Grignard or organolithium reagents are eliminated, (3) the only byproducts are hydrogen, which is easily removed, and the catalyst, which is present in low concentrations, can be recovered, (4) the process of the present invention tolerates a broad range of functional groups, (6) active catalysts are generated from common precursors and selectivities can be altered by adding commercially available ligands such as alkyl phosphines, (7) particular substitution patterns which are notoriously difficult to achieve using prior art aromatic substitution chemistry can be obtained in one step starting from inexpensive starting materials, and (8) Ir metal is relatively inert, Ir complexes generally have low toxicity, and Ir metal recovered from the reactions can be recovered from the reaction waste and recycled. Furthermore, the process can be used to make chiral borylated compounds.

The following examples are intended to promote a further understanding of the present invention.

EXAMPLE 1

This example shows the preparation of $\text{Ir}(\text{MesH})(\text{Bin})_3$ 9 from $(\text{Indenyl})\text{Ir}(\text{COD})$ 8 and excess HBPin in mesitylene.

(Indenyl)Ir(COD) 8 (2.54 g, 6.11 mmol) and
5 HBPin (3.91 g, 30.6 mmol) were dissolved in mesitylene (32 mL). The solution was then transferred to two glass bombs. The light brown solutions were then heated at 75° C for 64 h. The reaction mixture turned to dark brown after 24 h at 75° C. The solutions were
10 combined again. Mesitylene was removed by high vacuum leaving a viscous dark brown oil. The reaction mixture was then triturated with hexamethyldisiloxane (3 x 2 mL). After filtration and washed with cold hexamethyldisiloxane, a white solid was obtained (797
15 mg, 19%). $(\text{MesH})\text{Ir}(\text{BPin})_3$ 9: ^1H NMR (C_6D_6) δ 1.33 (s, 36 H, 3 $\text{BO}_2\text{C}_6\text{H}_{12}$), 2.23 (s, 9 H, 3 CH_3), 5.62 (s, 3 H, 3 CH). ^{11}B NMR (C_6D_6) δ 32.5. ^{13}C NMR (C_6D_6) δ 19.68, 25.73, 80.95, 96.97, 118.05. Elemental analysis for $\text{C}_{27}\text{H}_{48}\text{B}_3\text{IrO}_6$ calcd. C (46.77%), H (6.98%), N (0.00%).
20 Found C (47.13%), H (7.18%), N (0.02%).

EXAMPLE 2

This example shows the synthesis of precatalyst 12 in a NMR reaction.

25 $(\text{MesH})\text{Ir}(\text{BPin})_3$ 9 (10 mg, 0.014 mmol) was dissolved in C_6D_6 (400 μL) and dmpe solution (0.14 M in C_6D_6 , 100 μL , 0.014 mmol) was added. The reaction mixture was transferred to a J. Young NMR tube. After 36 h at room temperature, 12 was observed in ^1H , ^{11}B ,
30 and ^{31}P NMR. ^1H NMR (C_6D_6) δ 1.30 (s, 24 H, $\text{BO}_2\text{C}_6\text{H}_{12}$, 1.33 (s, 48 H, $\text{BO}_2\text{C}_6\text{H}_{12}$, 1.34 (unresolved d, 12 H), 1.39 (d, $^2J_{\text{HP}} = 4.5$ Hz, 24 H), 1.68 (d, $^2J_{\text{HP}} = 6.3$ Hz, 4 H),

1.73 (d, $^2J_{HP} = 6.6$ Hz, 4 H), 1.83 (unresolved d, 4 H).
 ^{11}B NMR (C_6D_6) δ 32.4 (br s). ^{31}P NMR (C^6D_6) δ -50.54
(unresolved t, 2 P), -10.85 (unresolved d, 4 P).

5

EXAMPLE 3

This example shows the synthesis of precatalyst 11 in a NMR reaction.

(MesH)Ir(BPin)₃ 9 (10 mg, 0.014 mmol) and bis-(di-tert-butylphosphino)ethane (dtBupe) (4.5 mg,
10 0.014 mmol) were dissolved in C_6H_{12} (500 μL) and transferred to a J. Young NMR tube. After 16 h at room temperature, 11 was observed in ^1H , ^{11}B and ^{31}P NMR. ^1H NMR (C_6H_{12}) δ 1.19 (s, 36 H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 1.28 (d, $^3J_{HP} = 12.0$ Hz, 36 H, $^t\text{Bu}_2\text{P}$), 1.84 (d, $^2J_{HP} = 10.7$ Hz, 4
15 H, $\text{PCH}_2\text{CH}_2\text{P}$). ^{11}B NMR (C_6H_{12}) δ 33.5 (br s). ^{31}P NMR (C_6H_{12}) δ 894.89.

EXAMPLE 4

This example shows the synthesis of
20 Preparation of fac-Ir(PMe₃)₃(BPin)₃.

PMe₃ (220 mg, 2.9 mmol) diluted in 2 mL C_6H_6 was added into a vial which was charged with (MesH)Ir(BPin)₃ (400 mg, 0.58 mmol) in 4 mL C_6H_6 . The reaction mixture was stirred at ambient temperature
25 for 30 minutes and the solvent was removed away under vacuum to give 461 mg fac-Ir(PMe₃)₃(BPin)₃ in quantitative yield. The product was recrystallized from concentrated pentane solution at -30° C to give colorless crystal. ^1H NMR (C_6H_6) δ 1.34 (s, 36 H, $\text{BO}_2\text{C}_6\text{H}_{12}$, 1.52 (m, 27 H, PMe₃). ^{11}B NMR (C_6H_6) δ 36.0.
30 $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6H_6) δ -64.

EXAMPLE 5

This example shows the synthesis of mer-Ir(PMe₃)₃(BPin)(H)(Ph).

HBPin (55 mg, 0.43 mmol) diluted in 2 mL
5 pentane was added into a vial which was charged with
Ir(PMe₃)₃Ph (194 mg, 0.39 mmol). The reaction mixture
was stirred at ambient temperature for 30 minutes and
the solvent was removed away under vacuum to give 241
mg mer-Ir(PMe₃)₃(BPin)(H)(Ph) in quantitative yield.
10 The product was recrystallized from concentrated
pentane solution at -30° C to give colorless crystal.
¹H NMR (C₆D₆) δ -11.32 (dt, 131 Hz, 20 Hz, 1 H,
hydride), 1.16 (s, 12H, BO₂C₆H₁₂), 1.41 (m, 27 H, PMe₃),
7.17-7.20 (m, 3 H), 7.98 (b, 2H). ¹¹B NMR (C₆D₆) δ
15 35.8. ³¹P{¹H} NMR (C₆D₆) δ -57.8 (t, 22.9 Hz, 1P), -
45.6 (d, 22.0 Hz, 2P). Calc. C (40.32), H (7.25).
Found C (39.95), H (7.38).

EXAMPLE 6

20 This example shows the synthesis of fac-Ir(PMe₃)₃(BPin)(H)(Me).

HBPin (27 mg, 0.195 mmol) diluted in 2 mL
pentane was added into a vial which was charged with
Ir(PMe₃)₄Me (100 mg, 0.21 mmol). The reaction mixture
25 was stirred at ambient temperature for 5 minutes and
the solvent was removed under vacuum to give orange
red color oily mixture of fac-Ir(PMe₃)₃(BPin)(H)(Me)
(83 %) and mer-Ir(PMe₃)₃(Me)(H)(BPin) (17 %) 94 mg in
75% yield. fac-Ir(PMe₃)₃(BPin)(H)(Me). ¹H NMR (C₆D₆) δ
30 -11.30 (dt, 140.4 Hz, 18.9 Hz, 1 H, hydride), 0.40 (m,
3H, Me), 1.25 (s, 12H, BO₂C₆H₁₂), 1.17 (d, 6.4 Hz, 9
H, PMe₃), 1.35 (d, 7.3 Hz, 9 H, PMe₃), 1.47 (d, 7.9 Hz,

9 H, PMe_3). ^{11}B NMR (C_6D_6) δ 38.6. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ -63.3 (br, 1P, PMe_3 trans to BPin), -56.83 (dd, 13.4 Hz, 23.2 Hz, 1P, PMe_3), -55.16 (dd, 13.4 Hz, 18.3 Hz, 1P, PMe_3). mer-Ir(PMe_3)₃(Me)(H)(BPin). ^1H NMR (C_6D_6) δ -11.98 (dt, 131.9 Hz, 23.0 Hz, 1H, hydride), -0.06 (m, 3H, Me), 1.19 (s, 12H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 1.14 (d, 29.9 Hz, 9 H, PMe_3 trans to hydride), 1.54 (t, 3.4 Hz, 18 H, 2 PMe_3 trans to each other). ^{11}B NMR (C_6D_6) δ 38.6. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ -57.8 (t, 1P, PMe_3 trans to hydride), -48.2 (d, 22.9 Hz, 2P, PMe_3 trans to each other).

EXAMPLE 7

This example shows the synthesis of (η^5 - C_5Me)Rh(PMe_3)(H)(BPin).

HBPin (486 mg, 3.8 mmol) diluted in 2 mL mesitylene was added into an air-free flask which was charged with $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{H})_2$ (400 mg, 1.26 mmol) in 8 mL mesitylene. The reaction mixture was heated at 110°C in an oil bath for 2.5 days. The solvent was removed under vacuum to give 480 mg $\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{H})(\text{BPin})$ as brown oil in 87% yield. ^1H NMR (C_6D_6) δ -13.94 (vt, 35.2 Hz, 1 H, hydride), 1.15 (s, 12H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 1.28 (dd, 9.8 Hz, 1.4 Hz, 9 H, PMe_3), 2.07 (m, 15 H, Cp^*). ^{11}B NMR (C_6D_6) 842.8. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ 6.3 (t, 166.3 Hz, 1P, PMe_3).

EXAMPLE 8

This example shows the synthesis of Ir(PMe_3)₄(BPin).

PMe_3 (161 mg, 2.1 mmol) diluted in 4 mL THF was added into the schlenk tube which was charged with mer,cis-Ir(PMe_3)₃(BPin)₂Cl (500 mg, 0.7 mmol) in 5 mL

THF. KOBU^t (158 mg, 1.4 mmol) dissolved in 5 mL THF was then added to the reaction mixture. The reaction mixture was stirred at room temperature for 90 minutes. The solvent was removed under vacuum. The product was extracted into 8 mL pentane, followed by concentrating filtrate to give 402 mg of $\text{Ir}(\text{PMe}_3)_4(\text{BPin})$ in 92% yield. The product was recrystallized from concentrated pentane solution at -30°C to give colorless crystal. ^1H NMR (C_6D_6) δ 81.24 (s, 12H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 1.58 (b, 36H, PMe_3). ^{11}B NMR (C_6D_6) δ 38. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ -57.5. Calc. C (34.67), H (7.76). Found C (34.76), H (7.89).

EXAMPLE 9

This example shows the synthesis of precatalyst 11 in a NMR reaction.

$\text{Ir}(\text{PMe}_3)_4\text{H}$ (15 mg, 0.03 mmol) was dissolved in C_6D_6 (332 μL) in a GC vial and transferred to a J. Young NMR tube. Additional C_6D_6 (166 μL) was used to wash the residue into the NMR tube. HBPin (4.4 μL , 0.03 mmol) was added into the NMR tube directly via microsyringe. At room temperature, the starting material was gradually converted into the mixture of *mer,cis*- $\text{Ir}(\text{PMe}_3)_3(\text{H})_2(\text{BPin})$ and *fac*- $\text{Ir}(\text{PMe}_3)_3(\text{H})_2(\text{BPin})$. The sample was allowed to stand at room temperature for 6 days, and *mer,cis*- $\text{Ir}(\text{PMe}_3)_3(\text{H})_2(\text{BPin})$ was gradually isomerized to give *fac*- $\text{Ir}(\text{PMe}_3)_3(\text{H})_2(\text{BPin})$ as the major species. *mer,cis*- $\text{Ir}(\text{PMe}_3)_3(\text{H})_2(\text{BPin})$. ^1H NMR (C_6D_6) δ -12.18 (dt, $J = 114.7, 23.2$ Hz, 1H, hydride trans to PMe_3), -10.46 (q, 1H, hydride trans to BPin), 1.21 (s, 12H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 1.49 (d, 9 H, PMe_3 trans to hydride),

1.69 (t, 3.5 Hz, 18 H, 2 PMe_3 trans to each other).
 ^{11}B NMR (C_6D_6) δ 38.6. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ -58.1 (t, 22.6 Hz, 1P), -48.1 (d, 22.6 Hz, 2P). fac-
 Ir(PMe_3)₃(H)₂(BPin). ^1H NMR (C_6D_6) δ -11.83
 5 (symmetrical second order m, 2H, hydride), 1.25 (s, 12H, $\text{BO}_2\text{C}_6\text{H}_{12}$, 1.32 (d, 7.0 Hz, 9 H, PMe_3 trans to BPin), 1.69 (d, 7.6 Hz, 18 H, 2 PMe_3 trans to hydride).
 ^{11}B NMR (C_6D_6) δ 38.6. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ -62.0 (br, 1P, PMe_3 trans to BPin), -54.59 (d, 23.2 Hz, 2P, PMe_3
 10 trans to hydride).

EXAMPLE 10

This example shows the generation of
 mer,trans-Ir(PMe_3)₃(BPin)₂(H) and fac-
 15 Ir(PMe_3)₃(BPin)₂(H) in a benzene- d_6 solution.

B_2Pin_2 (7.9 mg, 0.031 mmol) dissolved in C_6D_6
 (166 μL) was transferred to a J. Young NMR tube which
 was charged with Ir(PMe_3)₄H (15.4 mg, 0.031 mmol) in
 C_6D_6 (166 μL). Additional C_6D_6 (332 μL) was used to
 20 wash the residue into the NMR tube. The reaction
 mixture was then heated up at 60° C. The reaction was
 monitored by ^1H , ^{11}B , ^{31}P NMR spectra. The starting
 materials were gradually converted into the mixture of
 mer,trans-Ir(PMe_3)₃(BPin)₂(H) and fac-
 25 Ir(PMe_3)₃(BPin)₂(H). fac-Ir(PMe_3)₃(BPin)₂(H) was the
 major species after the temperature was taken up to
 100° C for 7 hours. mer,trans-Ir(PMe_3)₃(BPin)₂(H). ^1H
 NMR (C_6D_6) δ -12.36 (dt, J = 117 Hz, 21.7 Hz, 1H,
 hydride trans to PMe_3), 1.22 (s, 12H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 1.49
 30 (d, 8.0 Hz, 9H, PMe_3 trans to hydride), 1.74 (t, 3.4
 Hz, 18H, 2 PMe_3 trans to each other). ^{11}B NMR (C_6D_6) δ
 38.9. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ -59.6 (t, 22.0 Hz, 1P), -

50.8 (d, 22.0 Hz, 2P). fac-Ir(PMe₃)₃(BPin)₂(H). ¹H NMR (C₆D₆) δ -11.66 (dt, 118.1 Hz, 18.1 Hz, H, hydride trans to PMe₃), 1.29 (s, 24H, BO₂C₆H₁₂), 1.41 (vt, 18 H, 2 PMe₃ trans to BPin), 1.58 (d, 8.0 Hz, 9 H, PMe₃ trans to hydride). ¹¹B NMR (C₆D₆) δ 38.6. ³¹P{¹H} NMR (C₆D₆) δ -61.8 (br, 2P, PMe₃ trans to BPin), -56.6 (t, 22.0 Hz, 1P, PMe₃ trans to hydride).

EXAMPLE 11

10 This example shows the generation of Ir(PMe₃)₂(dppe)(BPin) in benzene-d₆.

dppe (8 mg, 0.02 mmol) dissolved in C₆D₆ (166 μL) was transferred to a J. Young NMR tube which was charged with Ir(PMe₃)₄(BPin) (12.5 mg, 0.02 mmol) in 15 C₆D₆ (166 μL). Additional C₆D₆ (166 μL) was used to wash the residue into the NMR tube. The reaction mixture was allowed to stand at room temperature for 3 days to give

Ir(PMe₃)₂(dppe)(BPin) as the major metal complex. ¹H NMR (C₆D₆) δ 1.10 (s, 12H, BO₂C₆H₁₂), 1.33 (t, 3.3 Hz, 18H, 2 PMe₃), 1.92-2.18 (m, 4H, CH₂), 6.98-7.12, 7.16-7.28, 7.72-7.89, 7.91-7.98 (m, 20 H, phenyl groups). ¹¹B NMR (C₆D₆) δ 38.8. ³¹P{¹H} NMR (C₆D₆) δ -58.9 (dd, 141.6 Hz, 26.8 Hz, 2P, PMe₃), 39.1 (td, 141.6 Hz, 13.4 25 Hz, 1P, PPh₂ cis to BPin), 46.1 (br, 1P, PPh₂ trans to BPin).

EXAMPLE 12

This example shows the catalytic synthesis 30 of 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolyl)-1,3-bis(trifluoromethyl)benzene from 1,3-bis(trifluoromethyl)benzene and excess HBPin using

precatalyst 8 and diphenylphosphinoethane (dppe).

Compound 8, (194 mg, 0.47 mmol) and dppe (186mg, 0.47 mmol) were dissolved HBPIn (4.5 g, 35 mmol). The solution was then added to a schlenk tube containing 1,3-bis(trifluoromethyl)benzene (5.0 g, 23.4 mmol). The reaction mixture was heated at 100° C in an oil bath for 22 h. The brown solid obtained was sublimed at 80° C (0.03 mmHg) to yield 1,3,5-C₆H₃(CF₃)₂(BPin) as a colorless solid (6.21 g, 78% based on 1,3-bis(trifluoromethyl)benzene).

EXAMPLE 13

This example shows the catalytic synthesis of 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolyl)-1,3-bis(trifluoromethyl)benzene from 1,3-bis(trifluoromethyl)benzene and excess HBPIn using precatalyst [Ir(COD)Cl]₂ and diphenylphosphinoethane (dppe).

[Ir(COD)Cl]₂ (157 mg, 0.47 mmol) and dppe (186mg, 0.47 mmol) were dissolved HBPIn (4.5 g, 35 mmol). The solution was then added to a schlenk tube containing 1,3-bis(trifluoromethyl)benzene (5.0 g, 23.4 mmol). The reaction mixture was heated at 100° C in an oil bath for 86 h. The brown solid obtained was sublimed at 80° C (0.03 mmHg) to yield 1,3,5-C₆H₃(CF₃)₂(BPin) as a colorless solid (6.84 g, 86% based on 1,3-bis(trifluoromethyl)benzene).

EXAMPLE 14

This example shows the catalytic synthesis of (4,4,5,5-Tetramethyl-1,3,2-dioxaborolyl)benzene from benzene and HBPIn using precatalyst 8 and

dimethylphosphinoethane (dmpe).

Precatalyst 8 (6.5 mg, 0.016 mmol) and dmpe (0.12 M in benzene, 127 μ L, 0.016 mmol) were dissolved in benzene (875 μ L). After 30 min at room temperature, the precatalyst solution was transferred to an air-free flask to which HBPIn (1.0 g, 7.8 mmol) and benzene (9 μ L) were added. The reaction mixture was heated at 150° C in an oil bath for 11 h. The pale brown solution was rotary evaporated to dryness. The brown viscous oil obtained was vacuum distilled to yield PhBPIn as a colorless viscous oil (1.45 g, 91%) at 66-67° C (0.03 mmHg).

EXAMPLE 15

This example shows the catalytic synthesis of (4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)benzene from benzene and HBPIn using [Ir(COD)Cl]₂ and dimethylphosphinoethane (dmpe).

[Ir(COD)Cl]₂ (5.2 mg, 0.016 mmol) and dmpe (0.016 M in benzene, 258 μ L, 0.016 mmol) were dissolved in benzene (740 μ L). After 30 min at room temperature, the precatalyst solution was transferred to an air-free flask to which HBPIn (1.0 g, 7.8 mmol) and benzene (9 μ L) were added. The reaction mixture was heated at 150° C in an oil bath for 6 h. The pale brown solution was rotary evaporated to dryness. The brown viscous oil obtained was vacuum distilled to yield PhBPIn as a colorless viscous oil (1.49 g, 93%) at 66-67° C (0.03 mmHg).

EXAMPLE 16

This example shows the catalytic synthesis

of 1,3,5-C₆F₃-2,4,6-(BPin)₃ from 1,3,5-trifluorobenzene and excess HBPIn using precatalyst 8 and dimethylphosphinoethane (dmpe) in cyclohexane.

5 Precatalyst 8 (8.7 mg, 0.021 mmol), dmpe solution (0.13 M in cyclohexane, 158 μ L, 0.021 mmol) and 1,3,5-trifluorobenzene (23 mg, 0.18 mmol) were dissolved in cyclohexane (440 μ L) and transferred to a J. Young NMR tube. The reaction mixture was heated at
10 150° C and monitored by ¹¹B, ¹⁹F, and ¹H NMR. ¹¹B NMR (C₆D₁₂) δ 28.32 (d, ¹J_{BH}= 175.1 Hz, HBPIn), 30.9 (sh, 1,3,5-C₆F₃-2,4,6-(BPin)₃). ¹⁹F NMR (C₆D₁₂) δ -107.53 (s, 3F, 1,3,5-C₆H₃F₃), -105.20 (s, 1F, 1,3,5-C₆H₂F₃-2-BPin), -96.52 (s, 2F, 1,3,5-C₆H₂F₃-2-BPin), -94.00 (s, 2F,
15 1,3,5-C₆HF₃-2,4-(BPin)₂), -84.45 (s, 1F, 1,3,5-C₆HF₃-2,4-(BPin)₂), -81.91 (s, 3F, 1,3,5-C₆F₃-2,4,6-(BPin)₃). After 17 h at 150° C, the reaction mixture was cooled to room temperature. 1,3,5-C₆H₃F₃-2,4,6-(BPin)₃ was precipitated as a colorless crystal (52 mg, 0.10
20 mmol). 1,3,5-C₆H₃F₃-2,4,6-(BPin)₃: ¹H NMR (CDCl₃) δ 1.31 (s, 36 H, BO₂C₆H₁₂). ¹³C NMR (CDCl₃) δ 24.70, 84.07, 173.10 (dt, ¹J_{CF}= 258.5 Hz, ³J_{CF}= 17.1 Hz). ¹⁹F NMR (CDCl₃) δ -83.31. ¹¹B NMR (CDCl₃) δ 29.1. MS (E.I.) m/z 510. Elemental analysis for C₂₄H₃₆B₃F₃O₆ calcd. C
25 (56.53%), H (7.11 %), N (0.00%). Found C (56.56%), H (7.09%), N (0.12%).

EXAMPLE 17

This example shows the catalytic synthesis
30 of (4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)benzene from benzene and HBPIn using precatalyst 8 and diphenylphosphinoethane (dppe) in cyclohexane

characterized by GC-FID.

Precatalyst 8 (2.9 mg, 7.0×10^{-3} mmol) and dppe (2.8 mg, 7.0×10^{-3} mmol) in cyclohexane (0.5 mL) were transferred to a J. Young NMR tube. Decane
5 (0.626 M in benzene, 50 μ L, 0.0313 mmol decane and 0.47 mmol benzene) and HBPIn (51 μ L, 0.35 mmol) were added. The reaction mixture was heated at 100° C and monitored by ^{11}B NMR. ^{11}B NMR (C_6D_6) δ 28.85 (d, $^1J_{\text{BH}} = 175.1$ Hz, HBPIn), 30.9 (br s, PhBPIn). After for 67 h at 100° C, a small aliquot of the reaction mixture was diluted with CH_2Cl_2 and a GC-FID chromatogram was obtained. PhBPIn (54% GC yield): GC-FID: 8.11 min (70° C, 2 min; 20° C/min; 250° C, 10 min). GC-MS: 7.71 min (70° C, 2
10 min; 20° C/min; 280° C, 10 min); (m/z) 204. ^1H NMR (CDCl_3) δ 1.35 (s, 12 H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 7.34-7.39 (m, 2H), 7.43-7.49 (m, 1 H), 7.81-7.84 (m, 2 H).

EXAMPLE 18

20 This example shows the catalytic synthesis of (4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)benzene from benzene and HBPIn using precatalyst 8 and dimethylphosphinoethane (dmpe) to generate 12 *in situ* and characterized by GC-FID.

25 Precatalyst 8 (2.9 mg, 7.0×10^{-3} mmol) was charged into a GC-vial in a glove box under N_2 . Decane (0.626 M in benzene, 50 μ L, 0.0313 mmol), HBPIn (51 μ L, 0.35 mmol), 1,2-bis(dimethylphosphino)ethane (0.0666 M in benzene, 105 μ L, 7.0×10^{-3} mmol) and
30 benzene (345 μ L) were added. The clear pale yellow solution was then transferred to a J. Young NMR tube. The reaction mixture was heated at 100° c and monitored

by ^{11}B and ^{31}P NMR. ^{11}B NMR (C_6H_6) δ 28.85 (d, $^1J_{\text{BH}} = 175.1$ Hz, HBPIn), 30.9 (br s, PhBPIn). ^{31}P NMR (C_6D_6) δ -51.01 (unresolved t, 2P), -11.05 (unresolved d, 4P). After 31 h at 100°C , a small aliquot of the reaction mixture was diluted with CH_2Cl_2 and a GC-FID chromatogram was obtained. PhBPIn (96% GC yield): GC-FID: 8.11 min (70°C , 2 min; $20^\circ\text{C}/\text{min}$; 250°C , 10 min). GC-MS: 7.71 min (70°C , 2 min; $20^\circ\text{C}/\text{min}$; 280°C , 10 min); (m/z) 204. ^1H NMR (CDCl_3) δ 1.35 (s, 12H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 7.34-7.39 (m, 2H), 7.43-7.49 (m, 1H), 7.81-7.84 (m, 2H).

EXAMPLE 19

This example shows the catalytic synthesis of (4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)benzene from benzene and HBPIn using precatalyst 9 and dimethylphosphinoethane (dmpe) to generate 12 *in situ* and characterized by GC-FID.

(MesH)Ir(BPin) $_3$ 9 solution (0.071 M in benzene, 100 μL , 7.0×10^{-3} mmol), dmpe solution (0.070 M in benzene, 100 μL , 7.0×10^{-3} mmol), decane solution (0.626 M in benzene, 50 μL , 0.0313 mmol), HBPIn (51 μL , 0.35 mmol) and benzene (250 μL) were mixed and transferred into a J. Young NMR tube was dissolved in C_6D_6 (400 μL) and dmpe solution (0.14 M in C_6D_6 , 100 μL , 0.014 mmol) was added. The reaction mixture was transferred to a J. Young NMR tube. The reaction mixture was heated at 100°C and monitored by ^{11}B and ^{31}P NMR. After for 177 h at 100°C , a small aliquot of the reaction mixture was diluted with CH_2Cl_2 and a GC-FID chromatogram was obtained. PhBPIn (97% GC yield): GC-FID: 8.11 min (70°C , 2 min; $20^\circ\text{C}/\text{min}$; 250°C , 10

min). GC-MS: 7.71 min (70° C, 2 min; 20° C/min; 280° C, 10 min); (m/z) 204. ¹H NMR (CDCl₃) 31.35 (s, 12 H, BO₂C₆H₁₂), 7.34-7.39 (m, 2H), 7.43-7.49 (m, 1H), 7.81-7.84 (m, 2H).

5

EXAMPLE 20

This example shows the catalytic synthesis of C₆H₄(OMe)(BPin) as an isomeric mixture from anisole and HBPIn using precatalyst 8 and trimethylphosphine characterized by GC-FID.

HBPIn (45 mg, 0.35 mmol) was charged into a J. Young NMR tube. Precatalyst 8 (Indenyl)Ir(COD) (2.9 mg, 7.0 x10⁻³ mmol) in anisole (0.5 mL) was added. PMe₃ (1.5
15 μL, 0.014 mmol) was added via a microsyringe. The reaction mixture was then heated at 150° C and monitored by ¹¹B NMR. ¹¹B NMR (C₆H₆) 328.66 (d, ¹J_{BH}= 175.1 Hz, HBPIn), 31.2 [br s, C₆H₄(OMe)BPin]. After heating for 29 h at 150° C, a small aliquot of the
20 reaction mixture was diluted with CH₂Cl₂ and a GC-FID chromatogram was obtained. The isomers, o-C₆H₄(OMe)(BPin):m-C₆H₄(OMe)(BPin):p-C₆H₄(OMe)(BPin) in a 9:74:17 ratio, were yielded (71 mg, 87%). GC-FID (70° C, 2 min; 20° C/min; 250° C, 10 min): 9.55 min (o-C₆H₄(OMe)(BPin)), 9.88 min (m-C₆H₄(OMe)(BPin)), 10.02
25 min (p-C₆H₄(OMe)(BPin)). GC-MS (70° C, 2 min; 20° C/min; 280° C, 10 min): 8.87 min, (m/z) 234 (o-C₆H₄(OMe)(BPin)); 9.14 min, (m/z) 234 (m-C₆H₄(OMe)(BPin)); 9.29 min, (m/z)
30 234 (p-C₆H₄(OMe)(BPin)).

EXAMPLE 21

This example shows the catalytic synthesis of 1,3,5-C₆F₃-2,4,6-(BPin)₃ from 1,3,5-trifluorobenzene and excess HBPIn using precatalyst 8 and dimethylphosphino-

5 ethane (dmpe) in neat.

Precatalyst 8 (29 mg, 0.07 mmol) and dmpe solution (10 mg, 0.07 mmol) were dissolved in HBPIn (1.5 g, 11.7 mmol) and transferred to an air-free flask. 1,3,5- Trifluorobenzene (310 mg, 2.34 mmol) was
10 added. The reaction mixture was heated at 150° C for 62 h. After cooled to room temperature, the reaction mixture was washed with pentane (5 x 5 mL). It was decanted and dried over high vacuum overnight. A colorless crystal was collected (911 mg, 76%). 1,3,5-
15 C₆H₃F₃-2,4,6-(BPin)₃: ¹H NMR (CDCl₃) δ 1.31 (s, 36 H, BO₂C₆H₁₂). ¹³C NMR (CDCl₃) δ 24.70, 84.07, 173.10 (dt, ¹J_{CF}= 258.5 HZ, ³J_{CF}= 17.1 HZ). ¹⁹F NMR (CDCl₃) δ -83.31. ¹¹B NMR (CDCl₃) δ 29.1. MS (E.I.) m/z 510. Elemental analysis for C₂H₃₆B₃F₃O₆ calcd. C (56.53%),
20 H(7.11%); N (0.00%). Found C (56.56%), H (7.09%), N (0.12%).

EXAMPLE 22

This example shows the catalytic synthesis
25 of 1,3-C₆B₃Cl₃BPIn) as an isomeric mixture from 1,3-dichlorobenzene and excess HBPIn using precatalyst 8 and diphenylphosphinoethane (dppe) in neat.

Precatalyst 8 (57 mg, 0.14 mmol) and dppe solution (54 mg, 0.14 mmol) were dissolved in HBPIn
30 (1.3 g, 10.2 mmol) and transferred to a schlenk tube. 1,3-

Dichlorobenzene (1.0 mg, 6.8 mmol) was added. The

reaction mixture was heated at 100° C for 14 h. The product ratio of 1,3,5-C₆H₃Cl₂BPin to another unidentified mono-borylated product, determined by GC-FID of the crude reaction mixture, was 97:3. After
5 removal of HBPin under high vacuum, the product was vacuum distilled at 93-94° C (0.03 mmHg). A colorless viscous oil obtained. It was further purified by washing with 100 mL H₂O (5 x 100 mL.) of the etherate solution of the product. After rotary evaporation and
10 dried over high vacuum, a colorless oil obtained (1.65 g, 89%). 1,3,5-C₆H₃Cl₂BPin: GC-FID: 10.40 min. 1 (70° C, 2 min.; 20° C/min.; 250° C, 10 min.). GC-MS: 9.73 min. (70° C, 2 min.; 20° C/min.; 280° C, 10 min.); (m/z) 272. ¹H NMR (CDCl₃) δ 1.32 (s, 12H, 13 BO₂C₆H₁₂),
15 7.41 (t, J= 2.0 Hz, 1H), 7.63 (d, J= 2.0 Hz, 2H). ¹³C NMR (CDCl₃) δ 24.82, 84.49, 131.06, 133.72, 134.72.

EXAMPLE 23

This example shows the catalytic synthesis
20 of (4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)benzene from benzene and HBPin using precatalyst 11 generated in situ and characterized by GC- FID.

Precatalyst 9 (4.9 mg, 7.0 x10⁻³ mmol) was charged into a GC-vial in a glove box under N₂. Decane
25 (0.626 M in benzene, 50 μL, 0.0313 mmol), HBPin (51 μL, 0.35 mmol), 1,2-bis(di-tert-butylphosphino)ethane (2.2 mg, 7.0 x10⁻³ mmol) and benzene (450 μL) were added. The clear pale yellow solution was then transferred to a J. Young NMR tube. The reaction
30 mixture was heated at 100° C and monitored by ¹¹B and ³¹P NMR. ¹¹B NMR (C₆H₆) δ 28.85 (d, ¹J_{BH}= 175.1 Hz, HBPin), 30.9 (br s, PhBPin). ³¹P NMR (C₆D₆) δ -51.01

unresolved t, 2P), -11.05 (unresolved d, 4P). After for 31 h at 100° C, a small aliquot of the reaction mixture was diluted with CH₂Cl₂ and a GC-FID chromatogram was obtained. PhBPin (11% GC yield): GC-FID: 8.11 min. (70° C, 2 min.; 20° C/min.; 250° C, 10 min.). GC-MS: 7.71 min. (70° C, 2 min.; 20° C/min.; 280° C, 10 min.); (m/z) 204. ¹H NMR (CDCl₃) δ 1.35 (s, 12 H, BO₂C~1z), 7.34-7.39 (m, 2H), 7.43-7.49 (m, 1H), 7.81-7.84 (m, 2H).

10

EXAMPLE 24

This example shows the catalytic synthesis of IC₆H₄(BPin) as an isomeric mixture from iodobenzene and HBPin using precatalyst 9 and dppe.

15 HBPin (485 µL, 3.34 mmol) was charged into an air-free flask. Precatalyst Ir(MesH)(BPin)₃ 9 (46 mg, 0.067 mmol) and dppe (27 mg, 0.067 mmol) were dissolved in iodobenzene (6.7 g, 33 mmol) and transferred to the
20 air-free flask. The reaction mixture was then heated at 100° C and monitored by ¹¹B NMR. ¹¹B NMR (C₆H₆) δ 27.5 (d, ¹J_{BH} = 175.1 Hz, HBPin), 28.5 (br s, IC₆H₄(BPin)). After heating for 57 h at 100° C, the reaction was
25 stopped. Iodobenzene was then vacuum distilled off at r.t. (0.03 mmHg). IC₆H₄(BPin) was vacuum distilled off at 93-95° C (0.03 mmHg) as a colorless viscous liquid. It was further purified by washing with H₂O (3 x 25 mL) the etherate solution. The organic layer was rotary
30 evaporated to dryness and vacuum dried. The isomers, m-C₆H₄I(BPin):p-C₆H₄I(BPin) in a 77:23 ratio, were yielded (852 mg, 77%). GC-MS (70° C, 2 min.; 20°

C/min.; 280° C, 10 min.): 10.12 min., (m/z) 330 *m*-C₆H₄I(BPin) and *p*-C₆H₄I(BPin) isomeric mixture. *m*-C₆H₄I(BPin): ¹H NMR (CDCl₃, 600 MHz) δ 1.32 (s, 12H, BO₂C₆H₁₂), 7.09 (unresolved dd, 1H), 7.72- 7.74 (m, 1H),
5 7.75-7.77 (m, 1H), 8.12 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 24.81, 84.05, 94.47, 129.58, 133.59, 140.02, 143.36. ¹¹B NMR (CDCl₃) δ 30.2. *p*-C₆H₄I(BPin): ¹H NMR (CDCl₃, 600 MHz) δ 1.31 (s, 12H, BO₂C₆H₁₂), 7.49 (d, *J*= 7.9 Hz, 2H), 7.70 (d, *J*= 7.9 Hz, 2H). ¹³C NMR (CDCl₃,
10 125 MHz) δ 24.81, 83.94, 98.77, 136.24, 136.85. ¹¹B NMR (CDCl₃) δ 30.2.

EXAMPLE 25

This example shows the catalytic synthesis
15 of 1,3,5-C₆H₃ClBr(BPin) from *m*-bromochlorobenzene and HBPIn using precatalyst 8 and dppe.

m-Bromochlorobenzene (501 mg, 2.6 mmol) was charged into an air-free flask. Precatalyst (Indenyl)Ir(COD) 8 (22 mg, 0.052 mmol) and dppe (21
20 mg, 0.052 mmol) were dissolved in HBPIn (570 μL, 3.9 mmol) and transferred to the air-free flask. The reaction mixture was then heated at 100° C and monitored by GC-FID. The reaction mixture was heated at 100° C for 17 h. The product ratio of 1,3,5-
25 C₆H₃ClBr(BPin) to another unidentified mono-borylated product, determined by GC-FID of the crude reaction mixture, was 99:1. After removal of HBPIn under high vacuum, the product was vacuum distilled at 98-99° C (0.03 mmHg). A colorless viscous oil obtained (735
30 mg, 89%) which solidified as a colorless crystal. 1,3,5-C₆H₃ClBr(BPin): GC-FID: 11.03 min. (70° C, 2 min.; 20° C/min.; 250° C, 10 min.). GC-MS: 10.22 min. (70°

C, 2 min.; 20° C/min.; 280° C, 10 min.); (m/z) 318. ¹H NMR (CDCl₃, 500 MHz) δ 1.32 (s, 12H, BO₂C₆H₁₂), 7.56 (unresolved dd, 1H), 7.67- 7.68 (m, 1H), 7.78 (m, 1H). ¹³C NMR (CDCl₃) δ 24.82, 84.51, 122.63, 133.13, 133.82, 5 134.85, 135.56. ¹¹B NMR (CDCl₃) δ 30.1.

EXAMPLE 26

This example shows the catalytic synthesis of Ph-BCat from benzene and HBCat using (Ind)Ir(COD).

10 (Ind)Ir(COD) (2.9 mg, 0.007 mmol) and dppe (2.8 mg, 0.007 mmol) were dissolved in C₆H₆ (166 μL) in a GC vial, and transferred to a J. Young NMR tube. HBCat (42 mg, 0.35 mmol) diluted in C₆H₆ (166 μL) was added into the NMR tube. Additional C₆H₆ (166 μL) was
15 used to wash the residue into the NMR tube. The reaction mixture was heated at 150° C in an oil bath. The conversion of the reaction was monitored by the disappearance of the resonance for HBCat in the ¹¹B NMR spectra. The product was confirmed by GC-MS. GC-MS
20 (m/z) 196.

EXAMPLE 27

This example shows the catalytic synthesis of Ph-BDAN from benzene and HBDAN using precatalyst
25 (Ind)Ir(COD).

(Ind)Ir(COD) (2.9 mg, 0.007 mmol) and dppe (2.8 mg, 0.007 mmol) were dissolved in C₆H₆ (332 μL) in a GC vial, and transferred to the J. Young NMR tube which was charged with HBDAN (58.6mg, 0.35 mmol).
30 Additional C₆H₆ (166 μL) was used to wash down the residue into the NMR tube. The reaction mixture was heated at 150° C in an oil bath. The conversion of the

reaction was monitored by the disappearance of the resonance for HBDAN in the ^{11}B NMR spectra. The product was confirmed by GC-MS. GC-MS (m/z) 244.

5

EXAMPLE 28

This example shows the catalytic synthesis of $\text{Ph-B}(\text{NH})_2\text{C}_6\text{H}_4$ from benzene and $\text{HB}(\text{NH})_2\text{C}_6\text{H}_4$ using precatalyst $(\text{Ind})\text{Ir}(\text{COD})$.

Compound $(\text{Ind})\text{Ir}(\text{COD})$ (2.9 mg, 0.007 mmol) and dppe (2.8 mg, 0.007 mmol) were dissolved in C_6H_6 (332 μL) in a GC vial, and transferred to the J. Young NMR tube which was charged with $\text{HB}(\text{NH})_2\text{C}_6\text{H}_4$ (41.1 mg, 0.35 mmol). Additional C_6H_6 (166 μL) was used to wash down the residue into the NMR tube. The reaction mixture was heated at 150°C in an oil bath. The conversion of the reaction was monitored by the disappearance of the resonance for $\text{HB}(\text{NH})_2\text{C}_6\text{H}_4$ in the ^{11}B NMR spectra. The product was confirmed by GC-MS. GC-MS (m/z) 194.

20

EXAMPLE 29

This example shows the catalytic synthesis of Ph-9-BBN from benzene and 9-BBN using precatalyst $(\text{Ind})\text{Ir}(\text{COD})$.

$(\text{Ind})\text{Ir}(\text{COD})$ (2.9 mg, 0.007 mmol) and dppe (2.8 mg, 0.007 mmol) were dissolved in C_6H_6 (332 μL) in a GC vial, and transferred to the J. Young NMR tube which was charged with 9-BBN (42.6mg, 0.35 mmol). Additional C_6H_6 (166 μL) was used to wash down the residue into the NMR tube. The reaction mixture was heated at 150°C in an oil bath. The conversion of the reaction was monitored by the appearance of the

resonance for Ph-9-BBN in the ^{11}B spectra. The product was further confirmed by comparing to authentic sample in GC-MS. GC-MS (m/z) 198.

5

EXAMPLE 30

This example demonstrates that benzotrifluoride is preferentially borylated in the presence of toluene by $\text{Ir}(\text{PMe}_3)_4(\text{BPin})$.

$\text{Ir}(\text{PMe}_3)_4(\text{BPin})$, (15 mg, 0.024 mmol) was dissolved in a pre-mixed 1:1 (mole/mole) of benzotrifluoride and toluene (332 μL) in a GC vial, and transferred to a J. Young NMR tube. Additional solvent mixture (166 μL) was used to wash the residue into the NMR tube. The reaction mixture was heated at 15 150°C in an oil bath. The conversion of the reaction was monitored by the disappearance of the resonance for $\text{Ir}(\text{PMe}_3)_4(\text{BPin})$ in the ^{11}B and ^{31}P NMR spectra. The isomer ratios were determined by the area ratio in the GC-FID chromatogram. The ratio of *m*-, *p*- $\text{C}_6\text{H}_4(\text{CF}_3)(\text{BPin})$:*o*-, *m*-, *p*- $\text{C}_6\text{H}_4(\text{Me})(\text{BPin})$ is 88:12.

20

EXAMPLE 31

This example demonstrates that benzotrifluoride is preferentially borylated in the presence of toluene using a solution of $(\text{MesH})\text{Ir}(\text{BPin})_3$ and trimethylphosphine.

$(\text{MesH})\text{Ir}(\text{BPin})_3$, (5 mg, 0.007 mmol) was dissolved in a pre-mixed 1:1 (mole/mole) of benzotrifluoride and toluene (332 μL) in a GC vial. 30 1.5 μL PMe_3 was added to the mixture via a microsyringe. The mixture was transferred to a J. Young NMR tube. Additional solvent mixture (166 μL)

was used to wash the residue into the NMR tube. Then
HBPIn (52 μ L, 0.36 mmol) was added to the NMR tube via
an autopipette. The reaction mixture was heated at
150° C in an oil bath. The conversion of the reaction
5 was monitored by the disappearance of the resonance
for pinacolborane in the ^{11}B NMR spectra. The isomer
ratios were determined by the area ratio in the GC-FID
chromatogram. The ratio of *m*-, *p*-C₆H₄(CF₃)(BPin) : *o*-,
m-, *p*-C₆H₄(Me)(BPin) is 94:6.

10

EXAMPLE 32

This example demonstrates that
benzotrifluoride is preferentially borylated in the
presence of toluene using a solution of (Ind)Ir(COD)
15 and trimethylphosphine.

(Ind)Ir(COD) (3 mg, 0.007 mmol) was
dissolved in a pre-mixed 1:1 (mole/mole) of
benzotrifluoride and toluene (332 μ L) in a GC vial.
1.5 μ L PMe₃ was added to the mixture via a
20 microsyringe. The mixture was transferred to a J.
Young NMR tube. Additional solvent mixture (166 μ L)
was used to wash the residue into the NMR tube. Then
HBPIn (52 μ L, 0.36 mmol) was added to the NMR tube via
an autopipette. The reaction mixture was heated at
25 150° C in an oil bath. The conversion of the reaction
was monitored by the disappearance of the resonance
for pinacolborane in the ^{11}B NMR spectra. The isomer
ratios were determined by the area ratio in the GC-FID
chromatogram. The ratio of *m*-, *p*-C₆H₄(CF₃)(BPin) : *o*-,
30 *m*-, *p*-C₆H₄(Me)(BPin) is 94:6.

EXAMPLE 33

This example shows the catalytic synthesis of (4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)benzene from benzene and HBPIn using precatalyst 11 generated *in situ* and characterized by GC-FID.

5 Precatalyst 9 (4.9 mg, 7.0×10^{-3} mmol) was charged into a GC-vial in a glove box under N_2 . Decane (0.626 M in benzene, 50 μ L, 0.0313 mmol), HBPIn (51 μ L, 0.35 mmol), 1,2-bis(di-tert-butylphosphino)ethane (2.2 mg, 7.0×10^{-3} mmol) and benzene (450 μ L) were
10 added. The clear pale yellow solution was then transferred to a J. Young NMR tube. The reaction mixture was heated at 150° C and monitored by ^{11}B and ^{31}P NMR. ^{11}B NMR (C_6D_6) δ 28.85 (d, $^1J_{BH} = 175.1$ Hz, HBPIn), 30.9 (br s, PhBPIn). ^{31}P NMR (C_6D_6) δ -51.01
15 (unresolved t, 2P), -11.05 (unresolved d, 4P). After for 31 h at 100° C, a small aliquot of the reaction mixture was diluted with CH_2Cl_2 and a GC-FID chromatogram was obtained. PhBPIn (74% GC yield): GC-FID: 8.11 min. (70° C, 2 min.; 20° C/min.; 250° C, 10
20 min.). GC-MS: 7.71 min. (70° C, 2 min.; 20° C/min.; 280° C, 10 min.); (m/z) 204. 1H NMR ($CDCl_3$) δ 1.35 (s, 12H, $BO_2C_6H_{12}$, 7.34-7.39 (m, 2H), 7.43-7.49 (m, 1H), 7.81-7.84 (m, 2H).

25

EXAMPLE 34

This example shows the catalysis by fac- $Ir(PMe_3)_3(BPin)_3$ in the presence of (MesH) $Ir(BPin)_3$.

(MesH) $Ir(BPin)_3$ (2.4 mg, 0.0035 mmol) and fac- $Ir(PMe_3)_3(BPin)_3$ (5.6 mg, 0.007 mmol) dissolved in C_6H_6
30 (300 μ L) were transferred into the J. Young NMR tube which was charged with decane (0.632 M in benzene, 50 μ L, 0.0316 mmol), and HBPIn (51 μ L, 0.35 mmol).

Additional C₆H₆ (150 µL) was used to wash the residue into the NMR tube. The reaction mixture was heated at 150° C in an oil bath. The conversion of the reaction was monitored by the disappearance of the resonance
5 for pinacolborane in the ¹¹B NMR spectra. After 16 hours at 150° C, a small aliquot of the reaction mixture was diluted with CH₂Cl₂ and a GC-FID chromatogram was obtained. PhBPin (91% GC yield).

10

EXAMPLE 35

This example shows the catalytic synthesis of (4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-benzene from benzene and HBPin using precatalyst 5.

Compound 4 (112 mg, 0.36 mmol) and HBPin
15 (277 mg, 2.17 mmol) were dissolved in was dissolved in 5 ml of benzene. The solution was transferred to a thick-walled reaction vessel, which was heated for 84 h at 120° C. Compound 4 was converted to compound 5 well before the onset of catalysis. Residual solvent
20 was removed from the reaction mixture and the residue was chromatographed on silica (CH₂Cl₂ eluant) to yield C₆H₅BPin as a colorless solid (153 mg, 0.760 mmol) in 34% yield based on HBPin.

25

EXAMPLE 36

This example shows the catalytic synthesis of 5-4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-1,3-bis(trifluoromethyl)benzene from 1,3-bis(trifluoromethyl)benzene and HBPin using
30 precatalyst 7.

Compound 7, (5 mg, 0.013 mmol) and HBPin (90 mg, 0.70 mmol) were dissolved in 550 µL 1,3-

bis(trifluoromethyl)benzene and heated at 150° C in a constant temperature circulator for 3 hours in a J. Young NMR tube. The solution was transferred to a vial and the solvent removed under vacuum at room temperature. The residue was chromatographed on a silica gel column, eluting with CH₂Cl₂, to yield 1,3,5-C₆H₃(CF₃)₂(BPin) as a colorless solid (203 mg, 86% based on HBPIn). C₆F₅(BPin). Catalytic addition of HBPIn to C₆HF₅ using solutions of compounds 1 or 7 gave C₆F₅(BPin) as a colorless solid (205 mg, 81% based on HBPIn, and 85 mg, 41 % based on HBPIn, for 1 and 3, respectively). mp 35-36° C. ¹H NMR (CDCl₃) δ 1.36 (s, 12H, BO₂C₆H₁₂). ¹¹B NMR (CDCl₃) δ 29. ¹⁹F NMR (CDCl₃) δ -129.5 (m, 2F), -149.7 (m, 1F), -161.9 (m, 2F). Calc. C. (49.02), H (4.11). Found C (48.33), H (4.59). GC-MS (m/z) 294.

EXAMPLE 37

This example shows the catalytic synthesis of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-1,3-dimethoxybenzene from 1,3-dimethoxybenzene and excess HBPIn using precatalyst 7 in cyclohexane.

Compound 7 (5.0 mg, 0.012 mmol), 1,3-dimethoxybenzene (97 mg, 0.70 mmol) and HBPIn (269 mg, 2.10 mmol) were dissolved in cyclohexane (1 mL) and transferred to an air-free flask. It was heated at 150° C and monitored by GC-FID. GC-FID (70° C, 2 min; 20° C/min; 250° C, 10 min): 6.49 min (1,3-C₆H₄(OMe)₂), 11.19 min (1,3,4-C₆H₃(OMe)₂(BPin)), 11.35 min (1,3,5-C₆H₃(OMe)₂(BPin)). The product ratio of 1,3,5-C₆H₃(OMe)₂(BPin):1,3,4-C₆H₃(OMe)₂(BPin), determined by

GC-FID of the crude reaction mixture, was 89:11. After heating for 32 h at 150° C the solvent was removed under vacuum at room temperature, and the residue was chromatographed on silica gel (60-200 mesh) column, using hexanes to hexanes:ethyl acetate (9:1) as the gradient eluant. Solvent removal gave 1,3,5-C₆H₃(OMe)₂(BPin) as a white solid (114 mg, 62% based on 1,3-dimethoxybenzene). mp 88-90° C. Rf= 0.40 (hexanes:ethyl acetate = 9:1). ¹H NMR (CDCl₃) δ 1.32 (s, 12H, BO₂C₆H₁₂), 3.79 (s, 6H, 2 OCH₃), 6.55 (t, J= 2.4 Hz, 1H), 6.93 (d, J= 2.4 Hz, 2H). ¹³C NMR (CDCl₃) δ 24.82, 55.40, 83.87, 104.50, 111.53, 160.35. ¹¹B NMR (CDCl₃) δ 30.8. Elemental analysis for C₁₄H₂₁BO₄ calcd.C (63.66%), H (8.01%), N (0.00%). Found C (63.58%), H (8.25%), N (0.01%). GC-MS (m/z) 264.

EXAMPLE 38

This example shows the catalytic synthesis of (4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)benzene from benzene and HBPin using precatalyst 7 in cyclohexane.

Compound 7 (5.0 mg, 0.012 mmol), benzene (109 mg, 1.4 mmol) and HBPin (45 mg, 0.35 mmol) were dissolved in cyclohexane (0.5 mL) and transferred to a J. Young NMR tube. The reaction was heated at 150° C and monitored by ¹¹B NMR. ¹¹B NMR (C₆H₁₂) δ 28.65 (d, ¹J_{BH}= 175.1 Hz, HBPin), 31.3 (br s, PhBPin). After heating for 38 h at 150° C, the solvent was removed under high vacuum at room temperature, and the residue was chromatographed on silica gel using hexanes as the eluant. PhBPin (42 mg, 59% based on HBPin) was isolated as a colorless oil. Rf = 0.17 (hexanes). ¹H

NMR (CDCl_3) δ 1.35 (s, 12 H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 7.34-7.39 (m, 2H), 7.43-7.49 (m, 1H), 7.81-7.84 (m, 2H). GC-MS (m/z) 204.

5

EXAMPLE 39

This example shows the catalytic synthesis of a mixture of (4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)benzene, 1,3-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)benzene, and 1,4-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)benzene from benzene and HBPIn using precatalyst 7 in cyclohexane.

Compound 7 (5.9 mg, 0.014 mmol), benzene (60 mg, 0.77 mmol), and HBPIn (90 mg, 0.70 mmol) were dissolved in cyclohexane (0.5 mL) and transferred to a J. Young NMR tube. The reaction was heated at 150°C and monitored by ^{11}B NMR. ^{11}B NMR (C_6H_{12}) δ 28.65 (d, $^1J_{\text{BH}} = 175.1$ Hz, HBPIn), 31.7 (br s, PhBPIn, 1,3- $\text{C}_6\text{H}_4(\text{BPIn})_2$ and 1,4- $\text{C}_6\text{H}_4(\text{BPIn})_2$). After heating for 87 h at 150°C , the solvent was removed under high vacuum at room temperature, and the residue was chromatographed on silica gel using hexanes as the eluant. PhBPIn (59 mg, 41% based on HBPIn) was isolated as a colorless oil. An isomer mixture of diborylated products $\text{C}_6\text{H}_4(\text{BPIn})_2$ was also isolated (39 mg, 33% based on HBPIn). $m\text{-C}_6\text{H}_4(\text{BPIn})_2:p\text{-C}_6\text{H}_4(\text{BPIn})_2 = 2:1$ (determined by ^1H NMR integrations). $m\text{-C}_6\text{H}_4(\text{BPIn})_2$: $R_f = 0.09$ (hexanes). ^1H NMR (CDCl_3) δ 1.32 (s, 24H, 2 $\text{BO}_2\text{C}_6\text{H}_{12}$), 7.36 (t, $J = 7.3$ Hz, 1H), 7.88 (dd, $J = 7.3, 1.4$ Hz, 2H), 8.26 (s, 1H). $p\text{-C}_6\text{H}_4(\text{BPIn})_2$: $R_f = 0.09$ (hexanes). ^1H NMR (CDCl_3) δ 1.33 (s, 24H, 2 $\text{BO}_2\text{C}_6\text{H}_{12}$, 7.79 (s, 4H).

EXAMPLE 40

This example shows the catalytic synthesis of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-1,3-bis(trifluoromethyl)benzene from 1,3-bis(trifluoromethyl)benzene and HBPIn using precatalyst 7 in cyclohexane.

Compound 7 (5.0 mg, 0.012 mmol), 1,3-bis(trifluoromethyl)benzene (75 mg, 0.35 mmol) and HBPIn (45 mg, 0.35 mmol) were dissolved in cyclohexane (0.5 mL) and transferred to a J. Young NMR tube. The reaction mixture was heated at 150° C and monitored by ¹¹B NMR. ¹¹B NMR (C₆H₁₂) δ 28.65 (d, ¹J_{BH} = 175.1 Hz, HBPIn), 30.8 (brs, 1,3,5-C₆H₃(CF₃)₂(BPin)). After heating for 10 h at 150° C, the solvent was removed under high vacuum at room temperature, and the residue was chromatographed on silica gel using CH₂Cl₂ as the eluant. 1,3,5-C₆H₃(CF₃)₂(BPin) was isolated as a colorless solid (105 mg, 88%). ¹H NMR (CDCl₃) 81.35 (s, 12H, BO₂C₆H₁₂, 7.93 (s, 1H), 8.22 (s, 1H). GC-MS (m/z) 340.

EXAMPLE 41

This example shows the catalytic synthesis of 1,3,5-C₆H₄Me₂(BPin) and 1,3-C₆H₃(CH₃)(CH₂BPin) as an isomeric mixture from m-xylene and HBPIn using precatalyst 7 in cyclohexane.

Compound 7 (10.0 mg, 0.025 mmol), m-xylene (75 mg, 0.70 mmol) and HBPIn (90 mg, 0.70 mmol) were dissolved in cyclohexane (0.5 mL) and transferred to a J. Young NMR tube. The reaction mixture was heated at 150° C and monitored by ¹¹B NMR. ¹¹B NMR (C₆H₁₂) δ 28.65 (d, ¹J_{BH} = 175.1 Hz, HBPIn), 31.1 (br s, 1,3,5-

$C_6H_3(CH_3)_2(BPin)$ and $1,3-C_6H_3(CH_3)(CH_2BPin)$. After heating for 59 h at $150^\circ C$, the solvent was removed under high vacuum at room temperature, and the residue was chromatographed on silica gel using hexanes as the eluant. The product ratio of $1,3,5-C_6H_3(CH_3)_2(BPin)$ and $1,3-C_6H_3(CH_3)(CH_2BPin)$, determined by GC-FID of the crude reaction mixture, was 94:6. $1,3,5-C_6H_3(CH_3)_2(BPin)$ and $1,3-C_6H_3(CH_3)(CH_2BPin)$ (91 mg, 56%) were isolated as a solid mixture of isomers. $1,3,5-C_6H_3(CH_3)_2(BPin)$: $R_f = 0.41$ (hexanes). 1H NMR ($CDCl_3$) 81.33 (s, 12H, $BO_2C_6H_{12}$), 2.30 (s, 6H, 2 CH_3), 7.09 (s, 1H), 7.42 (s, 1H). GC-MS (m/z) 232.

EXAMPLE 42

This example shows the catalytic synthesis of $1,2,4-C_6H_4(OMe)_2(BPin)$ from veratrole and HBPin using precatalyst 7 in cyclohexane.

Compound 7 (5.0 mg, 0.025 mmol), veratrole (97 mg, 0.70 mmol) and HBPin (90 mg, 0.70 mmol) were dissolved in cyclohexane (0.5 mL) and transferred to a J. Young NMR tube. The reaction mixture was heated at $150^\circ C$ and monitored by ^{11}B NMR. ^{11}B NMR (C_6H_{12}) δ 28.65 (d, $^1J_{BH} = 175.1$ Hz, HBPin), 31.4 (br s, $1,2,4-C_6H_3(OCH_3)_2(BPin)$). The product ratio of uncharacterized $1,2-C_6H_3(OMe)_2(BPin)$: $1,2,4-C_6H_3(OMe)_2(BPin)$, determined by GC-FID of the crude reaction mixture, was 98:2. After heating for 37 h at $150^\circ C$, the solvent was removed under high vacuum at room temperature, and the residue was chromatographed on silica gel using hexanes-ethyl acetate eluant gradient from 20:1 to 10:1. $1,2,4-C_6H_3(OCH_3)_2(BPin)$ was isolated as a colorless solid (118

mg, 64%). 1,2,4- $\text{C}_6\text{H}_3(\text{OCH}_3)_2(\text{BPin})$: mp 74-77° C. Rf = 0.23 (hexanes:ethyl acetate = 9:1). ^1H NMR (CDCl_3) δ 1.32 (s, 12H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 3.88 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.86 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 1.5 Hz, 1H), 7.40 (dd, J = 8.0, 1.5 Hz, 1H). ^{13}C NMR (CDCl_3) δ 24.82, 55.71, 55.81, 83.63, 110.42, 116.46, 128.52, 148.28, 151.59. ^{11}B NMR (CDCl_3) δ 30.3. Elemental analysis for $\text{C}_{14}\text{H}_{21}\text{BO}_4$ calcd. C (63.66%), H (8.01%), N (0.00%). Found C (63.41%), H (8.18%), N (0.01%).

GC-MS (m/z) 264.

EXAMPLE 43

This example shows the catalytic synthesis of 1,2,4- $\text{C}_6\text{H}_4(\text{OMe})_2(\text{BPin})$ from veratrole and excess HBPIn using precatalyst 7 in cyclohexane.

Compound 7 (10.0 mg, 0.025 mmol), veratrole (97 mg, 0.70 mmol) and HBPIn (270 mg, 2.1 mmol) were dissolved in cyclohexane (1 mL) and transferred to an air-free flask. The reaction mixture was heated at 150° C and monitored by GC-FID. GC-FID (70° C, 2 min; 20° C/min; 250° C, 10 min): 6.19 min (1,2- $\text{C}_6\text{H}_4(\text{OMe})_2$), 10.66 min (uncharacterized 1,2- $\text{C}_6\text{H}_3(\text{OMe})_2(\text{BPin})$), 11.27 min (1,2,4- $\text{C}_6\text{H}_3(\text{OMe})_2(\text{BPin})$). The product ratio of uncharacterized 1,2- $\text{C}_6\text{H}_3(\text{OMe})_2(\text{BPin})$: 1,2,4- $\text{C}_6\text{H}_3(\text{OMe})_2(\text{BPin})$, determined by GC-FID of the crude reaction mixture, was 99:1. After heating for 45 h at 150° C, the solvent was removed under high vacuum at room temperature, and the residue was chromatographed on silica gel using hexanes-ethyl acetate eluant gradient from 20:1 to 10:1. 1,2,4- $\text{C}_6\text{H}_3(\text{OCH}_3)_2(\text{BPin})$ was isolated as a colorless solid (153 mg, 82%).

EXAMPLE 44

This example shows the catalytic synthesis of 1,3,5-C₆H₄(OCH₃)(CH₃)(BPin) from 3-methylanisole and excess HBPIn using precatalyst 7 in cyclohexane.

Compound 7 (15.0 mg, 0.037 mmol), 3-methylanisole (86 mg, 0.70 mmol) and HBPIn (113 mg, 0.88 mmol) were dissolved in cyclohexane (1 mL) and transferred to an air-free flask. The reaction mixture was heated at 150° C and monitored by GC-FID. GC-FID (70° C, 2 min; 20° C/min; 250° C, 10 min): 4.92 min (1,3-C₆H₄(OCH₃)(CH₃)), 10.23 min (uncharacterized 1,3-C₆H₃(OCH₃)(CH₃)(BPin)), 10.45 min (1,3,5-C₆H₃(OCH₃)(CH₃)(BPin)), 10.57 min (uncharacterized 1,3-C₆H₃(OCH₃)(CH₃)(BPin)). The product ratio of 1,3,5-C₆H₃(CH₃)(OCH₃)(BPin) to other unidentified monoborylated products, determined by GC-FID of the crude reaction mixture, was 92:5:3. After heating for 25 h at 150° C, the solvent was removed under high vacuum at room temperature, and the residue was chromatographed on silica gel using hexanes to hexanes-ethyl acetate (20:1) as the gradient eluant. 1,3,5-C₆H₃(OCH₃)(CH₃)(BPin) (93 mg, 54%) was isolated as a colorless solid after chromatographed on silica gel using hexanes to hexanes:ethyl acetate (20:1) as the gradient eluant. 1,3,5-C₆H₃(OCH₃)(CH₃)(BPin): mp 55-56° C. R_f = 0.52 (hexanes:ethyl acetate = 20:1). ¹H NMR (CDCl₃) δ 1.33 (s, 12H, BO₂C₆H₁₂), 2.31 (s, 3H, CH₃), 3.80 (s, 3H, OCH₃), 6.82 (m, 1H), 7.11 (d, J= 2.5 Hz, 1H), 7.22 (m, 1H). ¹³C NMR (CDCl₃) δ 21.21, 24.83, 55.23, 83.76, 115.48, 118.79, 128.01, 138.91, 159.13. ¹¹B NMR (CDCl₃) δ 30.9. Elemental analysis for C₁₄H₂₁BO₃

calcd. C (67.77%), H (8.53%), N (0.00%). Found C (67.54%), H (8.53%), N (0.02%). GC-MS (m/z) 248.

EXAMPLE 45

5 This example shows the catalytic synthesis of 1,3,5- $C_6H_4(OCH_3)(NMe_2)(BPin)$ from *m*-N,N-dimethylanisidine and excess HBPIn using precatalyst 7 in cyclohexane.

Compound 7 (10.0 mg, 0.025 mmol), *m*-N,N-dimethylanisidine (90 mg, 0.60 mmol) and HBPIn (305 mg, 2.38 mmol) were dissolved in cyclohexane (1 mL) and transferred to an air-free flask. The reaction mixture was heated at 150° C and monitored by GC-FID. GC-FID (70° C, 2 min; 20° C/min; 250° C, 10 min): 7.65 min (1,3- $C_6H_4(OCH_3)(NMe_2)$), 12.40 min (1,3,5- $C_6H_3(OCH_3)(NMe_2)(BPin)$), 12.60 min (uncharacterized 1,3- $C_6H_3(OCH_3)(NMe_2)(BPin)$). The product ratio of 1,3,5- $C_6H_3(OCH_3)(NMe_2)(BPin)$ to another unidentified monoborylated product, determined by GC-FID of the crude reaction mixture, was 95:5. After heating for 19 h at 150° C, the solvent was removed under high vacuum at room temperature, and the residue was sublimed (0.03 mmHg, 80° C). 1,3,5- $C_6H_3(OCH_3)(NMe_2)(BPin)$ was isolated as a colorless solid (124 mg, 75%). 1,3,5- $C_6H_3(OCH_3)(NMe_2)(BPin)$: mp 64-66° C. R_f = 0.33 (hexanes:ethyl acetate = 9:1). 1H NMR ($CDCl_3$) δ 1.32 (s, 12H, $BO_2C_6H_{12}$), 2.93 (s, 6H, NMe_2), 3.81 (s, 3H, OCH_3), 6.37 (unresolved dd, 1H), 6.70 (d, J = 2.2 Hz, 1H), 6.82 (d, J = 2.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.81, 40.72, 55.26, 83.65, 102.90, 106.22, 112.27, 151.59, 160.14. ^{11}B NMR ($CDCl_3$) δ 30.8. Elemental analysis for $C_{15}H_{24}BNO_3$ calcd. C (65.00%), H (8.73%), N (5.05%).

Found C (65.25%), H (8.98%), N (4.86%). GC-MS (*m/z*) 277.

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EXAMPLE 46

This example shows the catalytic synthesis of 1,3,5- $\text{C}_6\text{H}_3(\text{NMe}_2)_2(\text{BPin})$ from *m*-N,N,N,N-tetramethylphenylenediamine and excess HBPIn using precatalyst 7 in cyclohexane.

10 Compound 7 (15.0 mg, 0.037 mmol), *m*-N,N,N,N-tetramethylphenylenediamine (115 mg, 0.70 mmol) and HBPIn (269 mg, 2.10 mmol) were dissolved in cyclohexane (1 mL) and transferred to an air-free flask. The reaction mixture was heated at 150° C and
15 monitored by GC-FID. GC-FID (70° C, 2 min; 20° C/min; 250° C, 10 min): 9.07 min (1,3- $\text{C}_6\text{H}_4(\text{NMe}_2)_2$), 13.35 min (1,3,5- $\text{C}_6\text{H}_3(\text{NMe}_2)_2(\text{BPin})$), 13.53 min (uncharacterized 1,3- $\text{C}_6\text{H}_3(\text{NMe}_2)_2(\text{BPin})$). The product ratio of 1,3,5- $\text{C}_6\text{H}_3(\text{NMe}_2)_2(\text{BPin})$ to another unidentified mono-borylated
20 product, determined by GC-FID of the crude reaction mixture, was 97:3. After heating for 28 h at 150° C, the residue was filtered off and recrystallized from hot cyclohexane. 1,3,5- $\text{C}_6\text{H}_3(\text{NMe}_2)_2(\text{BPin})$ was isolated as a colorless solid (140 mg, 69%). 1,3,5- $\text{C}_6\text{H}_3(\text{NMe}_2)_2(\text{BPin})$: mp 178-180° C. Rf= 0.22
25 (hexanes:ethyl acetate = 5:1). ^1H NMR (CDCl_3) δ 1.32 (s, 12H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 2.94 (s, 12H, 2 NMe_2), 3.81 (s, 3 H, OCH₃), 6.23 (t, *J* = 2.2 Hz, 1 H), 6.65 (d, *J* = 2.2 Hz, 2H). ^{13}C NMR (CDCl_3) δ 24.81, 41.05, 83.43, 1.01.30,
30 108.77, 151.38. ^{11}B NMR (CDCl_3) δ 31.0. HRMS for $\text{C}_{16}\text{H}_{27}\text{BN}_2\text{O}_2$ calcd. 290.2169, found 290.2167. GC-MS (*m/z*) 290.

EXAMPLE 47

This example shows the catalytic synthesis of N-ⁱPr₃Si-pyrrole-3-BPin from N-ⁱPr₃Si-pyrrole and excess HBPIn using precatalyst 7 in cyclohexane.

Compound 7 (10.0 mg, 0.025 mmol), N-tri-isopropylsilylpyrrole (156 mg, 0.70 mmol) and HBPIn (269 mg, 2.10 mmol) were dissolved in cyclohexane (1 mL) and transferred to an air-free flask. The reaction mixture was heated at 150° C and monitored by GC-FID. GC-FID (70° C, 2 min; 20° C/min; 250° C, 10 min): 8.85 min (N-ⁱPr₃Si-pyrrole), 12.86 min (uncharacterized N-ⁱPr₃Si-pyrrole-BPin), 13.05 min (N-ⁱPr₃Si-pyrrole-3-BPin). The product ratio of N-ⁱPr₃Si-pyrrole-3-BPin to another unidentified mono-borylated product, determined by GC-FID of the crude reaction mixture, was 99:1. After heating for 41 h at 150° C, the solvent was removed under high vacuum at room temperature, and the residue was chromatographed on silica gel using hexanes to hexanes:ethyl acetate (20:1) as the gradient eluant. N-ⁱPr₃Si-pyrrole-3-BPin (199 mg, 81%) was isolated as a colorless oil. N-ⁱPr₃Si-pyrrole-3-BPin: R_f = 0.43 (hexanes:ethyl acetate = 20:1). ¹H NMR (CDCl₃) δ 1.06 (d, J = 7.3 Hz, 18H, 6 CH₃), 1.30 (s, 12H, BO₂C₆H₁₂), 1.44 (septet, J = 7.3 Hz, 3H, 3 CH), 6.60 (dd, J = 2.7, 1.2 Hz, 1H), 6.79 (dd, J = 2.7, 2.0 Hz, 1H), 7.21- 7.22 (unresolved dd, 1H). ¹³C NMR (CDCl₃) δ 11.62, 17.78, 24.84, 82.69, 115.57, 124.96, 133.65. ¹¹B NMR (CDCl₃) δ 30.5. HRMS for C₁₆H₂₇BN₂O₂ calcd. 349.2612, found 349.2602. GC-MS (m/z) 290.

EXAMPLE 48

This example shows the catalytic synthesis of 1-trimethylsilyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane from N-trimethylsilylpyrrole and HBPIn using precatalyst 7 and characterized by GC-MS.

5 Precatalyst 7 (5 mg, 0.012 mmol) and HBPIn (45 mg, 0.35 mmol) were dissolved in N-trimethylsilylpyrrole (0.5 mL) and was transferred to a J. Young NMR tube in a glove box under N₂. The reaction mixture was heated at 150° C and monitored by
10 ¹¹B NMR. ¹¹B NMR (C₆H₆) δ 28.85 (d, ¹J_{BH}= 175.1 Hz, HBPIn), 34.2 (br s, TMSBPIn). After for 8 h at 150° C, a small aliquot of the reaction mixture was diluted with CH₂Cl₂ and a GC-MS chromatogram was obtained. TMSBPIn (90% GC yield). GC-MS: 5.00 min. (70° C, 2
15 min.; 20° C/min.; 280° C, 10 min.): (m/z) 201.

EXAMPLE 49

In this example a two-step, one-pot protocol for the synthesis of a biaryl from an arene, a borane, and a halogenated aromatic is demonstrated. An
20 arylboronate ester is first generated using an Ir catalyst, and is then subsequently coupled to the halogenated aromatic using a palladium catalyst.

To a small Schlenk tube equipped with a stir
25 bar, in a glove box, was added HBPIn (224 mg, 1.75 mmol) to mixture of 1,3-bis(trifluoromethyl)benzene (250 mg, 1.17 mmol), Ir(COD)(Indenyl) (9.7 mg, 0.023 mmol), and dppe (9.3 mg, 0.23 mmol). The tube was sealed and heated at 100° C for 6 h. The reaction
30 solution was allowed to cool to room temperature and Pd(PPh₃)₄ (27.0 mg, 0.234 mmol), iodobenzene (217 mg, 1.06 mmol), Ba(OH)₂•8H₂O (552 mg, 1.75 mmol), and

toluene (10 mL) were added. The mixture was stirred at 90-95° C for 16.5h. The mixture was allowed to cool, additional Ba(OH)₂·8H₂O (200 mg, 0.634 mmol) was added, and the solution stirred for 2 h at 90-95° C.

5 Solvent was removed by rotary evaporation and the crude material subjected to column chromatography eluting with hexanes. 3,5-Bis(Trifluoromethyl)biphenyl was obtained (46 mg, 15%) as a colorless oil. The assignment was verified by comparison to the GC

10 retention time and ¹H NMR data to an authentic sample prepared from 3,5-bis(trifluoromethyl)phenyl pinacolborane and iodobenzene. ¹H NMR (CDCl₃, 300 MHz) 8.00 (s, 2H), 7.93 (s, 1H), 7.85-7.58 (m, 2H), 7.53-7.42 (m, 3H).

15

EXAMPLE 50

This example shows the catalytic synthesis of N-3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)phenyl-2,5-dimethylpyrrole and HBPIn in

20 cyclohexane using precatalyst 8 and dimethylphosphinoethane (dmpe).

N-3-Chlorophenyl-2,5-dimethylpyrrole (535 mg, 2.6 mmol) was charged into an air-free flask. (Indenyl)Ir(COD) 8 (21 mg, 0.05 mmol), dmpe (7.5 mg, 0.05 mmol) and HBPIn (1.0 g, 7.8 mmol) in cyclohexane

25 (5 mL) was added. The reaction mixture was then heated at 100° C for 44 h. N-3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)phenyl-2,5-dimethylpyrrole (93% GC-yield): GC-MS: 12.04 min. (70° C, min.; 20° C min⁻¹; 280° C, 10 min.); (m/z) 331. ¹H

30 NMR (CDCl₃) δ 1.32 (s, 12H, BO₂C₆H₁₂), 2.00 (s, 6H, CH₃), 5.85 (s, 2H, pyrrolic protons), 7.29 (unresolved

dd, 1H), 7.49-7.50 (m, 1H), 7.77-7.78 (m, 1H). ¹¹B NMR (CDCl₃) δ 30.5.

EXAMPLE 51

5 In this example a two-step, one-pot protocol for the synthesis of a biaryl from an arene, a borane, and a halogenated aromatic is demonstrated. An arylboronate ester is first generated using an Ir catalyst, and is then subsequently coupled to the
10 halogenated aromatic using a palladium catalyst.

 Biphenyl: Closed system: To a J. Young NMR tube, in a glove box, was added benzene (437 mg, 5.60 mmol), Ir(COD)(indenyl) (3.0 mg, 0.0070 mmol), dppe (2.8 mg, 0.0070 mmol), dodecane (internal
15 standard, 11.5 mg, 0.0675 mmol), and HBPin (45 mg, 0.352 mmol). The tube was sealed, removed from the box, and stirred at 100° C for 18h. The tube was allowed to cool to room temperature and Pd(PPh₃)₄ (8.1 mg, 0.007 mmol), K₃PO₄ (112 mg, 0.528 mmol), PhI (72.7
20 mg, 0.356 mmol), and DME (2 mL) were added. A GC-trace of the reaction mixture revealed PhBPin in 85.7% yield. Three freeze-pump-thaw cycles were performed to remove residual O₂ and the reaction mixture was heated at 80° C for 2 days. GC analysis showed
25 biphenyl (81.8% GC-yield), iodobenzene (7.9.7% GC-conversion), and PhBPin (79.1% GC-conversion).

EXAMPLE 52

 In this example a two-step, one-pot protocol
30 for the synthesis of a biaryl from an arene, a borane, and a halogenated aromatic is demonstrated. An arylboronate ester is first generated using an Ir

catalyst, and is then subsequently coupled to the halogenated aromatic using a palladium catalyst.

Open system: To a Schenk tube, in a glove box, was added benzene (1.0 mL, 11.2 mmol),
5 Ir(COD)(indenyl) (3.0 mg, 0.0070 mmol), dppe (2.8 mg, 0.0070 mmol), dodecane (internal standard, 12.0 mg, 0.070 mmol), and HBPIn (45 mg, 0.352 mmol). The tube was sealed, removed from the box, and stirred at 100° C for 18 h. The tube was allowed to cool to room
10 temperature and Pd(PPh₃)₄ (8.5 mg, 0.0074 mmol), K₃PO₄ (112 mg, 0.528 mmol), PhI (74.9 mg, 0.367 mmol), and DME (2 mL) was added. A GC-trace of the reaction mixture revealed PhBPIn in 78.9% yield. The reaction mixture was degassed by purging with N₂ and heated at
15 80° C for overnight. GC analysis showed biphenyl (97.3% GC-yield), iodobenzene (84.1% GC-conversion), and PhBPIn (90.7% GC-conversion).

EXAMPLE 53

20 A comparison of precatalysts Cp*(PMe₃)Ir(H)(BPin) (2) and Cp*Rh(η^4 -C₆Me₆) (7) in borylations of various substituted arenes revealed that the Ir system was more selective towards arene C-H activation (Cho et al., J. Am. Chem. Soc. 122:
25 12868-12869 (2000)). Given the importance of selectivity in chemical synthesis, these findings spurred a detailed investigation of the original Ir system. Those results are described herewith.

Compound 2 is stable in benzene solutions
30 after prolonged thermolysis, which eliminates several mechanistic possibilities, including PMe₃ dissociation to generate Cp*Ir(H)(BPin), an analog of proposed




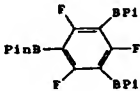

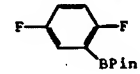

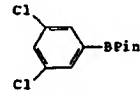

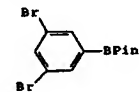

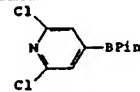



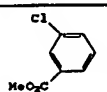
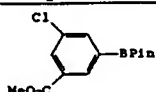
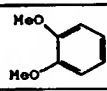
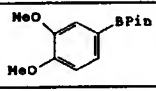
intermediates in the Rh system. However, added PMe_3 strongly inhibits catalysis where HBPIn is present. This indicated that small quantities of phosphine- Ir^{V} species could be active. Since $\text{Cp}^*\text{IrH}_{4-x}(\text{BPin})_x$ species (x = 1, 2) form in the thermolysis of Cp^*IrH_4 and HBPIn (Kawamura and Hartwig, J. Am. Chem. Soc. 123: 8422-8423 (2001)), anisole borylations with identical loadings of Cp^*IrH_4 and 2 were compared. From this experiment, $\text{Cp}^*\text{IrH}_{4-x}(\text{BPin})_x$ intermediates can be eliminated because they are not kinetically competent for catalysis and the borylation regioselectivities for Cp^*IrH_4 and 2 differ substantially. At 150° C, the following isomer ratios were obtained for anisole borylation with 20 mol% precatalyst loadings: Cp^*IrH_4 , o:m:p = 3:49:48; 2 o:m:p = 2:79:19.

Exclusion of a simple phosphine dissociative pathway narrows the plausible catalysts to two choices: (i) Ir phosphine species arising from Cp^* loss or (ii) species where both Cp^* and PMe_3 have been lost. The latter possibility was intriguing in light of Marder's synthesis of $(\eta^6\text{-arene})\text{Ir}(\text{BCat})_3$ complexes (Cat = ortho-catecholate) from $(\text{Ind})\text{Ir}(\text{COD})$ (8, Ind $\eta^5\text{-C}_9\text{H}_7$, COD = 1,5-cyclooctadiene) and HBCat in arene solvents. Using an analogous route, we prepared $(\eta^6\text{-mesitylene})\text{Ir}(\text{BPin})_3$ (9 wherein $\text{B}(\text{OR})^2$ is BPin) in 19% yield from $(\text{Ind})\text{Ir}(\text{COD})$ and HBPIn (Compound 9 has been prepared as an analytically pure white solid. Relevant spectroscopic data included ^1H NMR (C_6D_6) δ 1.33 (s, 36 H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 2.23 (s, 9H, $\text{C}_6\text{H}_3(\text{CH}_3)_3$), 5.62 (s, 3H, $\text{C}_6\text{H}_3(\text{CH}_3)_3$). ^{11}B NMR (C_6D_6) δ 32.5. ^{13}C NMR (C_6D_6) δ 19.68, 25.73, 80.95, 96, 97, 118.05). Compound 9 reacted with benzene at 150° C to produce Ir metal and

three equivalents of C_6H_5BPin , but did not catalyze C_6H_5BPin formation from benzene and $HBPin$. Thus, it appears that phosphines or related donor ligands are required for catalysis.

5 Utilizing the lability of the mesitylene ligand in **9**, Ir phosphine species were generated *in situ* from **9** and appropriate phosphines and subsequently screened for activity. Borylation using 2 mol% **9** and 4 mol% PMe_3 was viable (Table 2, entry 1),
10 and both catalytic activity and TONs for benzene borylation increased dramatically relative to precatalyst **2**. Borylation rates were appreciable when $[P]:[Ir] < 3:1$, but decreased dramatically when $[P]:[Ir]$ ratio equals or exceeds 3:1.

15 The low isolated yields of **9** hampered screening efforts and precluded practical applications despite the dramatic improvement in catalytic activity. Hence, we sought alternative means for generating active catalysts. Since NMR spectra
20 indicated quantitative generation of **9** from **8**, *in situ* generation of active catalysts by phosphine addition to **8** was examined. Compound **8** was synthesized in 86% yield from indenyl lithium and $[IrCl(COD)_2]$ (Merola and Kacmarcik, *Organometallics* **8**: 778- 784 (1989)). This
25 approach was successful and results for benzene borylations are shown in Table 2 (entries 2-5). Chelating phosphines substantially increased activity and TONs as highlighted for 1,2-bis(dimethylphosphino)ethane ($dmpe$) where the
30 effective TON of 4500 (Table 2, entry 5) represented an improvement of more than 1000-fold over precatalyst **2**.

Ent.	Sub.	Arene : HBPIn	Prod.	Cat.	Lig- and	Temp (°C)	Time (h)	Yield %
1	C ₆ H ₆	16:1	PhBPIn	(MesH) Ir (BPIn) ₃ (9)	PMe ₃	150	15	98 ^b
2	C ₆ H ₆	16:1	PhBPIn	(Ind) Ir (COD) (8)	PMe ₃	150	18	88 ^b
3	C ₆ H ₆	16:1	PhBPIn	8	dppe	150	2	95 ^b
4	C ₆ H ₆	16:1	PhBPIn	8	dmpe	150	2	84
5	C ₆ H ₆	16:1	PhBPIn	0.02 mol% 8	dmpe	150	61	90 ^b
6	C ₆ H ₆	16:1	PhBPIn	(IrCl(COD)) ₂	dmpe	150	8	74 ^b
7		4:1		8	dmpe	150	1	63
8		1:5		8	dmpe	150	62	76
9		4:1		8	dppe	100	3	81
10		1:1.5		8	dppe	100	14	89
11		1:1.5		8	dppe	100	17	92
12 ^c		1:2		8	dppe	100	4	69
13		10:1	--	8	dppe	100	60	--
14		10:1	 m: p=79:21	9	dppe	100	57	77
15 ^c		1:2		8	dppe	100	25	95
16		1:3		8	dmpe	150	95	82

^aReactions run in neat arene, Ir= 2 mol%, P:Ir=2:1, and yields are reported for isolated materials unless otherwise noted. (COD= 1,5,-cyclooctadiene, dmpe= Me₂PCH₂CH₂PMe₂, dppe= Ph₂PCH₂CH₂PPh₂).

^bGC yield based on HBPIn. ^cReactions run in cyclohexane.

In addition, active catalysts were generated from commercially available sources such as $[\text{IrCl}(\text{COD})]_2$ (Table 2, entry 6).

5 If the primary active species generated by PMe_3 addition to 8 and 9 are identical to those generated from 2, borylations of substituted benzenes should exhibit similar regio- and chemoselectivities. Anisole is a useful substrate for probing
10 regioselectivity and the *meta:para* ratios determined from borylations by active species generated by PMe_3 addition to 8 and 9 are similar to those for 2 (For catalysts generated from 4 mol% PMe_3 and 2 mol% 8 or 9, the following isomer ratios were obtained for anisole
15 borylation at 150° C: 8, *o:m:p* = 9:74:17; 9, *o:m:p* = 8:75:17. For 8 and 9, *ortho* borylation increases slightly, which could signify a minor pathway that is not accessible from 2).

To assess chemoselectivities, the ratios of
20 arene to benzylic activation in *m*-xylene were examined. The selectivities of catalysts generated from 8 (13:1) and 9 (12:1) were diminished relative to the selectivity of precatalyst 2 (35:1). Nevertheless, the Ir catalysts were more selective for
25 arene activation than the Rh catalyst, 7, where the selectivity was 7:1 (Cho et al., J. Am. Chem. Soc. 122: 12868-12869 (2000)); a Rh catalyst that is highly selective for benzylic borylation has been recently reported (Shimada et al., Angew. Chem., Int. Ed. 40:
30 2168-2171 (2001)), and the addition of one equivalent of the chelating phosphine, 1,2-bis(diphenylphosphino)ethane (dppe) per equivalent of

8 or 9 generated catalysts where the arene to benzylic selectivities exceeded 142:1.

Dramatic differences in chemoselectivities between Ir and Rh catalysts were found for halogenated substrates, where the Ir catalysts preferentially activated C-H bonds. A representative procedure for borylation is given for entry 10 of Table 2. Briefly, in a glove box under N₂, compound 8 (57 mg, 0.14 mmol) and dppe (54 mg, 0.14 mmol) were dissolved in HBPin (1.30 g, 10.2 mmol). The solution was transferred to a thick-walled air-free flask containing 1,3-dichlorobenzene (1.00 g, 6.80 mmol). The clear yellow solution was heated at 100° C under N₂ and monitored by GC-FID. After 14 hours, the reaction mixture was pumped down to obtain a brown oil, which was vacuum distilled at 93-94° C (0.03 mmHg). The resulting oil was then dissolved in Et₂O (10 mL) and washed with water (5 x 100 mL). After drying over MgSO₄, ether was removed under high-vacuum to give 1.65 g (89% yield) of colorless 1,3,5-C₆H₃Cl₂BPIn (mp 36-38° C: ¹H NMR (500 MHz, CDCl₃) δ 1.32 (s, 12H), 7.41 (t, J= 2.0 Hz, 1H), 7.63 (d, J=2.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 24.82, 84.49, 131.1, 133.7, 134.7. ¹¹B NMR (CDCl₃) δ 30). Good yields of mono- or tri-borylated products of 1,3,5-trifluorobenzene were obtained by adjusting the arene:HBPin ratio (Table 2, entries 7 and 8). In contrast, previous attempts to effect multiple borylations of 1,3,5-trifluorobenzene using the Rh catalyst 7 led to increased defluorination (Cho et al., J. Am. Chem. Soc. 122: 12868-12869 (2000)). Borylations of aromatics with heavier halogen substituents provided an even starker contrast between

Ir and Rh catalysts. For example, Ir catalyzed borylations of 1,3-dichlorobenzene and 1,3-dibromobenzene generate meta functionalized products in high yields (entries 10 and 11), while
5 dehalogenation is the dominant pathway in Rh catalyzed reactions. Dechlorination was observed during attempted silylations of 1,3-dichlorobenzene using closely related Rh catalysts (Ezbiensky et al., Organometallics 17: 1455-1457 (1998)). The finding
10 that aromatic C-halogen bonds survived in the Ir catalyzed reactions contrasted the Pd-catalyzed reactions of boranes and aryl bromides where the C-Br bonds were converted to C-B or C-H bonds (Murata, et al., J. Org. Chem. 65: 164-168 (2000)). Entry 12 of
15 Table 2 illustrates an extension of meta selective borylation to a halogenated heterocycle.

Since aryl iodides have the weakest carbon-hydrogen bonds, they are most susceptible towards reductive cleavage by transition metals. Hence, it is
20 not surprising that the Ir catalysts generated from 8 were ineffective in aromatic borylation of iodobenzene (Table 2, entry 13). However, iodobenzene and HBPIn reacted smoothly to yield a mixture of C₆H₄I(BPin) isomers when active catalysts were generated from the
25 Ir^{III} source, 9, and dppe (Table 2, entry 14). Thus, Ir catalysts are compatible with the entire range of aryl halides. Furthermore, functional group tolerance that was previously found in Rh catalyzed borylations extends to Ir catalyzed reactions (viz., ester
30 compatibility in entry 15 of Table 2) and Ir selectively borylates symmetrical 1,2-substituted arenes at the 4-position (Table 2, entry 16).

From a mechanistic standpoint, catalytic cycles involving oxidative addition/reductive elimination from $\text{Ir}^{\text{I/III}}$ and/or $\text{Ir}^{\text{III/V}}$ intermediates are consistent with the results herein. Within this context, we considered Ir^{I} and Ir^{III} boryl intermediates to be the most likely C-H activating species in the $\text{Ir}^{\text{I/III}}$ and $\text{Ir}^{\text{III/V}}$ cycles, respectively. Hence, the Ir^{I} and Ir^{III} boryl complexes, $\text{Ir}(\text{BPin})(\text{PMe}_3)_4$ and *fac*- $\text{Ir}(\text{BPin})_3(\text{PMe}_3)_3$, were prepared in order to evaluate their stoichiometric reactions with arenes.

Compounds $\text{Ir}(\text{BPin})(\text{PMe}_3)_4$ and *fac*- $\text{Ir}(\text{BPin})_3(\text{PMe}_3)_3$ have been fully characterized as shown by the following spectroscopic data: $\text{Ir}(\text{BPin})(\text{PMe}_3)_4$, ^1H NMR (C_6D_6 , 25°C) δ 1.24 (s, 12H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 1.58 (b, 36H, PCCH_3) $_3$. ^{11}B NMR (C_6D_6) δ 38. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ -57.5; *fac*- $\text{Ir}(\text{BPin})_3(\text{PMe}_3)_3$, ^1H NMR (C_6D_6) δ 1.34 (s, 36H, $\text{BO}_2\text{C}_6\text{H}_{12}$), 1.52 (m, 27H, $\text{P}(\text{CH}_3)$) $_3$. ^{11}B NMR (C_6D_6) δ 36.0. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ -64. In reactions with arenes, compounds $\text{Ir}(\text{BPin})(\text{PMe}_3)_4$ and *fac*- $\text{Ir}(\text{BPin})_3(\text{PMe}_3)_3$ both reacted cleanly with benzene to produce PhBPin and the corresponding hydride complexes shown in Equations 2 and 3 (Figures 4A and 4B, respectively), which was consistent with the idea that Ir^{I} or Ir^{III} species can effect arene borylation; however, the arene products from stoichiometric reactions of $\text{Ir}(\text{BPin})(\text{PMe}_3)_4$ and *fac*- $\text{Ir}(\text{BPin})_3(\text{PMe}_3)_3$ with iodobenzene differed substantially. Specifically, compound $\text{Ir}(\text{BPin})(\text{PMe}_3)_4$ reacted rapidly with iodobenzene at room temperature, but isomers of $\text{C}_6\text{H}_4\text{I}(\text{BPin})$ were not detected, even after prolonged thermolysis. Conversely, thermolysis of *fac*- $\text{Ir}(\text{BPin})_3(\text{PMe}_3)_3$ in iodobenzene produced *m*- and *p*-

$\text{C}_6\text{H}_4\text{I}(\text{BPin})$ in 54% yield, based on $\text{Ir}(\text{BPin})_3(\text{PMe}_3)_3$, in addition to a 45% yield of PhBPin .

Since conversion rates in catalytic reactions plummet when $[\text{P}]:[\text{Ir}]$ ratios equal or exceed 3:1, the observation that $\text{Ir}(\text{BPin})(\text{PMe}_3)_4$ and *fac*- $\text{Ir}(\text{BPin})_3(\text{PMe}_3)_3$ were not kinetically competent for catalysis was expected. However, this does not exclude the possibility that identical intermediates are generated in the stoichiometric and catalytic reactions. Instead, generation of appropriate intermediates under catalytic conditions could simply be more efficient. Nevertheless, the stoichiometric transformations lend credence to either Ir^{I} or Ir^{III} species mediating C-H activations under catalytic conditions. The reactions of $\text{Ir}(\text{BPin})(\text{PMe}_3)_4$ and *fac*- $\text{Ir}(\text{BPin})_3(\text{PMe}_3)_3$ with iodobenzene have greater mechanistic implications. For example, the absence of $\text{C}_6\text{H}_4\text{I}(\text{BPin})$ products in thermolysis of $\text{Ir}(\text{BPin})(\text{PMe}_3)_4$ mirrored the failed attempt to borylate iodobenzene using the Ir^{I} precatalyst 8 (Table 2, entry 13). The reactivity of $\text{Ir}(\text{BPin})_3(\text{PMe}_3)_3$ suggests that an Ir^{III} intermediate may activate C-H bonds in the presence of C-I bonds, but the chemistry of $\text{Ir}(\text{BPin})(\text{PMe}_3)_4$ is more important because it essentially excludes the participation of Ir^{I} species in the successful borylation of iodobenzene using the Ir^{III} precatalyst 9 (Table 2, entry 14).

In summary, an investigation of the original Ir catalytic system, whose promising selectivities could not be practically implemented due to extremely low effective TONs, has produced a family of efficient borylation catalysts with remarkable regio- and

chemoselectivities. In addition to providing a direct route to aryl and heteroaryl boron compounds from boranes and arenes, the viability of a tandem catalytic cascade where the first step is an Ir
5 catalyzed aromatic borylation has been demonstrated.

EXAMPLE 54

This example provides a protocol for performing Rh catalyzed aromatic borylations in
10 cyclohexane. Borylation at the 5-position of several 1,3-substituted aromatic species ranging from electron-rich (1,3-(NMe₂)₂C₆H₄) to electron-deficient (1,3-(CF₃)₂C₆H₄) yields the corresponding aryl boronate esters. Veratrole was selectively borylated at the 4-
15 position, thus extending regioselectivity to 1,2-substituted benzenes. Selective borylation at the 3-position of an N-protected pyrrole has also been demonstrated, providing a valuable reagent for cross-coupling reactions in a single step.

20 We have developed a simple protocol for preparing arylboronate esters in good to moderate yields where the aromatic substrate is the limiting reagent. In addition, we have expanded the scope of selective meta borylation of 1,3-substituted benzenes
25 and have extended the borylation chemistry to protected pyrrole.

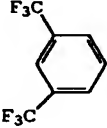
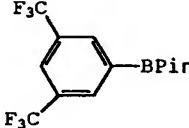
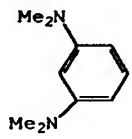
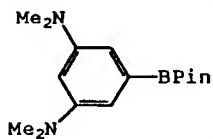
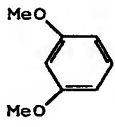
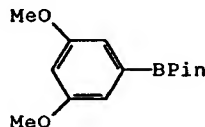
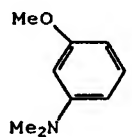
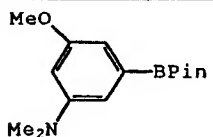
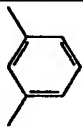
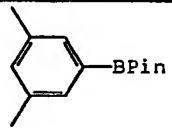
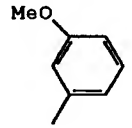
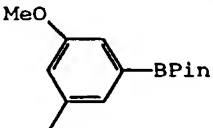
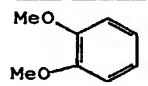
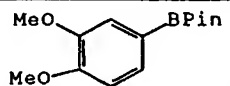
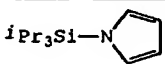
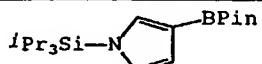
For this study, we used Hartwig's precatalyst, Cp*Rh(η^4 -C₆Me₆) (4) (Chen et al., Science 2000, 287, 1995-1997) whose reactivity we compared to
30 Ir precatalysts that were utilized for the catalytic aromatic borylation of C-H bonds. Although the Ir precatalysts seem to be more selective, their

effective turnover numbers were too low for practical applications. The preferential activation of the stronger aryl C-H bonds in the presence of weaker benzylic C-H bonds is significant, particularly in
5 light of Marder and co-worker's recent report of selective benzylic borylation using the precatalyst trans-Rh(Cl)(PiPr₃)₂(N₂) (Shimada et al., Angew. Chem., Int. Ed. 2001, 40, 2168-2171).

Since solutions of 4 do not readily borylate
10 secondary or tertiary C-H positions, cyclohexane was an obvious choice for an inert solvent. Indeed, catalytic borylations in cyclohexane using 2 mol % of 4 with a modest excess of pinacolborane (HBPin) gave boronate esters in reasonable yields (Table 3).
15 Reactions were performed in sealed vessels at 150° C until ¹¹B NMR spectra indicated that most of the borane had been consumed. Crude mixtures were analyzed by GC-MS and the reported yields are for isolated products. In cases where isomers were produced,
20 compounds were separated by chromatography, unless otherwise noted.

We have found that trace solvent impurities can inhibit catalytic borylations. With the exception of benzene, the substrates have been selected to test
25 the generality of sterically directed borylation.

For benzene three sets of conditions were employed (Table 3, entries 1-3). In the first case, borylation was examined with equimolar quantities of benzene and HBPin.

Table 3				
Entry	Arene	HBPin: arene	Time	Product (yield)
1	C_6H_6	1:4	36 h	PhBPIn (59)
2 ^a	C_6H_6	1:1	57 h	PhBPIn (41) <i>m</i> -, <i>p</i> - C_6H_4 (BPIn) ₂ (33, <i>m</i> : <i>p</i> =2:1)
3 ^b	C_6H_6	4:1	61 h	<i>m</i> - C_6H_4 (BPIn) ₂ <i>p</i> - C_6H_4 (BPIn) ₂ 1,3,5- C_6H_3 (BPIn) ₂
4		1:1	10 h	 (88)
5		3:1	28 h	 (69)
6 ^c		3:1	32 h	 (62)
7		4:1	19 h	 (75)
8 ^d		1:1	59 h	 (53)
9		1.2:1	25 h	 (54)
10		3:1	45 h	 (82)
11		3:1	41 h	 (81)

^aDiborylated isomers were not separated; ^bisomer mixture containing small amounts of PhBPIn; ^c1,2,3-(OMe)₂C₆H₃(BPIn) was isolated in 2% yield; ^d*m*-C₆H₄(Me)(CH₂BPIn) was isolated in 6% yield.

The isolated yields of products based on borane as the limiting reagent are 41% for PhBPin and 33% for $C_6H_4(BPin)_2$ both as a 2:1 mixture of meta and para isomers. Using a 4:1 ratio of benzene to borane, diborylation is minimized and PhBPin can be isolated in 59% yield. If a moderate excess of HBPin is used, the major species in the crude reaction mixture are *m*- $C_6H_4(BPin)_2$, *p*- $C_6H_4(BPin)_2$, and 1,3,5- $C_6H_3(BPin)_3$ in an approximate 1.0:1.2:1.7 ratio as determined from GC and NMR data. Further purification was not attempted; however, comparison of the weight of the crude mixture (311 mg) to the combined weights of HBPin, C_6H_6 , and catalyst (340 mg) indicates efficient conversion to borylated species.

In cyclohexane solvent, 1,3-substituted arenes yield 1,3,5-substituted aryl boronate esters as major products (entries 4-9). Reactivities for arene substrates were similar except for 1,3- $(CF_3)_2C_6H_4$, which was substantially more reactive. In a previous report (Cho et al., J. Am. Chem. Soc. 2000, 122, 12868-12869), significant benzylic activation was observed in neat *m*-xylene. To determine whether acceptable yields for methyl-substituted arenes could be obtained, 1 equiv of HBPin was used for the borylation of *m*-xylene in cyclohexane. The aryl and benzyl boronate esters were separated, with the aryl product being favored by a factor of about 9:1. For 3-methylanisole, a modest excess of HBPin was used and the 1,3,5-substituted major product was readily obtained in 54% yield after chromatography. Entries 7 and 9 demonstrate that preference for borylation at the 5-position holds for unsymmetrically substituted

arenes. We attempted the borylation of *m*-dichlorobenzene and found a mixture of products with unreacted arene, chlorobenzene, $\text{ClC}_6\text{H}_4(\text{BPin})$, and $\text{Cl}_2\text{C}_6\text{H}_4(\text{BPin})$ isomers as the major species. This is not surprising since we previously observed competitive C-H and C-F activation using the same precatalyst for borylations of fluorinated arenes (Cho et al., J. Am. Chem. Soc. 2000, 122, 12868-12869. Consequently, no other halogenated arenes were examined. An attempted borylation of benzonitrile led to nitrile reduction instead of aromatic C-H activation.

Entries 10 and 11 represent extensions of directed borylations to 1,2-substituted arenes and pyrrole. For veratrole, two isomers were detected by GC in a 99:1 ratio with the expected major product being 1,2,4- $\text{C}_6\text{H}_3(\text{OMe})_2(\text{BPin})$. After chromatographic purification, the major isomer was isolated in 82% yield. Direct borylations of pyrrole and trimethylsilyl pyrrole were ineffective. However, selective borylation at the less hindered 3-position could be achieved by increasing the steric bulk of the silyl protecting group. The regiochemistry of the borylation was verified by preparing the known phenyl-substituted pyrrole (Alvarez et al., J. Org. Chem. 1992, 57, 1653-1656) via the Suzuki coupling of the pyrrolyl boronate ester with IC_6H_5 .

The pyrrole result represents an important extension of the arene chemistry because selective functionalization at the 3-position is considerably more difficult than at the 2-position. For example, the best reported synthesis of 3- $^i\text{Pr}_3\text{SiNC}_4\text{H}_3(\text{B}(\text{OH})_2)$

involves iodination of ${}^1\text{Pr}_3\text{SiNC}_4\text{H}_4$ by N-iodosuccinamide to afford $3-{}^1\text{Pr}_3\text{SiNC}_4\text{H}_3\text{I}$, generation of the lithiated pyrrole with tBuLi , quenching with B(OMe)_3 , and hydrolytic workup to afford the boronic acid in 27%
5 yield from ${}^1\text{Pr}_3\text{SiNC}_4\text{H}_4$ (Alvarez et al., J. Org. Chem. 1992, 57, 1653-1656). In a single step, the reaction in entry 11 of Table 3 provides a stable source of the boronic acid in 81% yield.

In summary, we have shown that cyclohexane
10 can serve as an inert solvent for Rh-catalyzed borylations of arenes. In addition, selective borylation at the 5-position of 1,3-substituted arenes has been demonstrated for a broader range of substrates, including dimethyl resorcinol and 1,3-
15 $(\text{NMe}_2)_2\text{C}_6\text{H}_4$ where functionalizations at the 5-position are difficult. An example of regioselective borylation of a symmetric, 1,2-substituted arene has been demonstrated for veratrole. Last, ${}^1\text{Pr}_3\text{SiNC}_4\text{H}_4$ has been selectively borylated at the less hindered 3-
20 position in high yield.

While the present invention is described herein with reference to illustrated embodiments, it should be understood that the invention is not limited hereto. Those having ordinary skill in the art and
25 access to the teachings herein will recognize additional modifications and embodiments within the scope thereof. Therefore, the present invention is limited only by the claims attached herein.

WE CLAIM:

-1-

A catalytic composition comprising:

- 5 an iridium or rhodium complex with three or more substituents, excluding hydrogen, bonded to the iridium or rhodium.

-2-

A catalytic composition comprising:

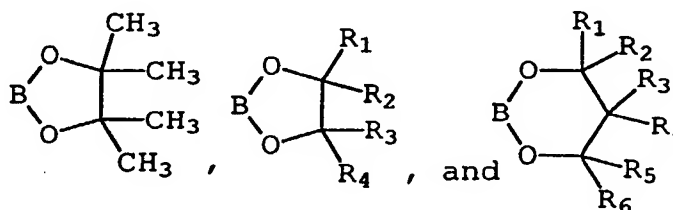
- an iridium or rhodium complex with three or more substituents, excluding hydrogen, bonded to the iridium or rhodium and a ligand selected from the group consisting of a phosphorus organic ligand, an organic amine, an imine, a nitrogen heterocycle, and an ether in a molar ratio between about 1 to 3 and 1 to 1, wherein the ligand is at least in part bonded to the iridium or rhodium.
- 5

-3-

- The catalytic composition of Claim 2 wherein the phosphorus organic ligand is selected from the group consisting of trimethyl phosphine (PMe_3), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,2-bis(diphenylphosphino)ethane (dppe).
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-4-

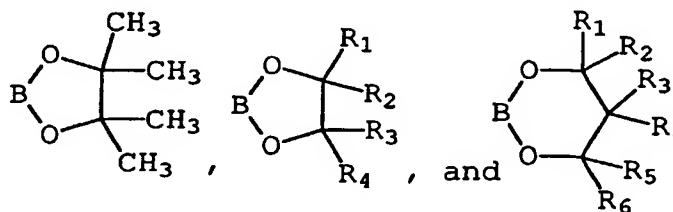
The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(ArH)Ir(BY)_3$ wherein ArH is selected from the group consisting of aromatic, heteroaromatic, polyaromatic, and heteropolyaromatic hydrocarbon; and BY is a boron moiety of the formula



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

-5-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(MesH)Ir(BY)_3$ wherein MesH is mesitylene; and BY is a boron moiety selected from the group consisting of



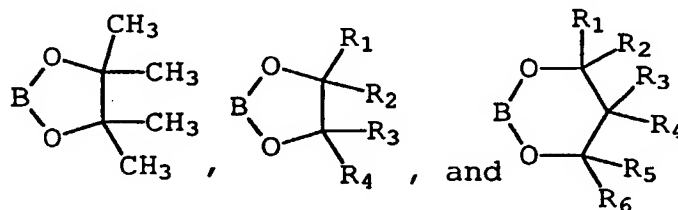
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wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl

containing 1 to 8 carbons, and a carbon in a cyclic structure.

-6-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(P(Y_4)(Y_5)(Y_6))_3Ir(H)_n(BY)_{3-n}$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; n is 0, 1, or 2; and BY is a boron moiety selected from the group consisting of

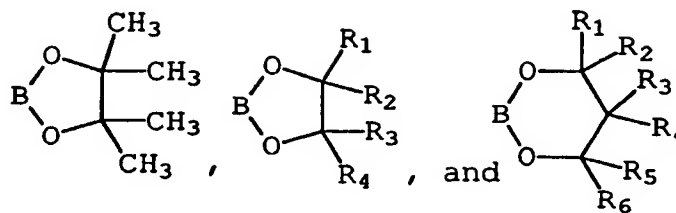


wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

-7-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(P(R_{14})(R_{15})(R_{16}))_3Ir(H)_n(BY)_{3-n}$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; n

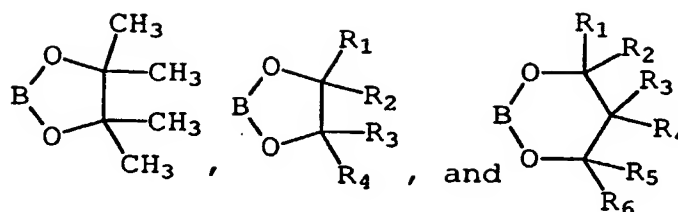
is 0, 1, or 2; and BY is a boron moiety selected from the group consisting of



wherein R₁, R₂, R₃, R₄, R₅, and R₆ are each selected
 5 from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

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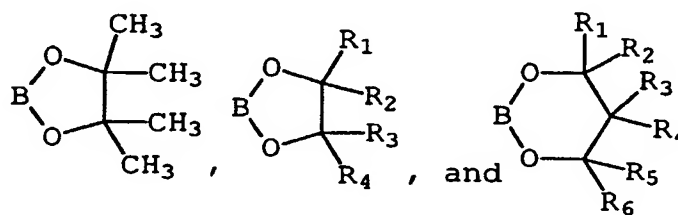
The catalytic composition of Claim 1 or 2 wherein the iridium complex is (P(Y₄)(Y₅)(Y₆))₃Ir (H)(R₁₇)(BY) wherein Y₄, Y₅, and Y₆ are each selected from the group consisting of hydrogen, halide, alkyl,
 5 aryl, alkoxide (-O(R₁₁)), and amide (-N(R₁₂)(R₁₃)) wherein R₁₁, R₁₂, and R₁₃ are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; R₁₇ is
 10 selected from the group consisting of a linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure; and BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

-9-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(P(R_{14})(R_{15})(R_{16}))_3Ir(H)(R_{17})(BY)$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; R_{17} is selected from the group consisting of a linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure; and BY is a boron moiety selected from the group consisting of

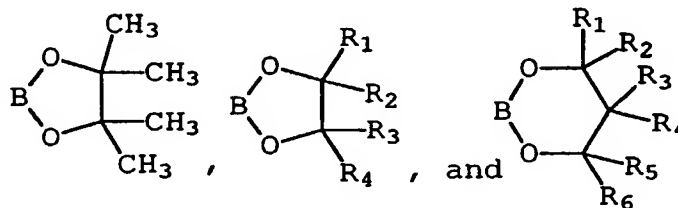


wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

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-10-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $\{(\text{PY}_7\text{P})\text{Ir}(\text{BY})_3\}_2(\mu_2-(\text{PY}_7\text{P}))$ wherein BY is a boron moiety selected from the group consisting of

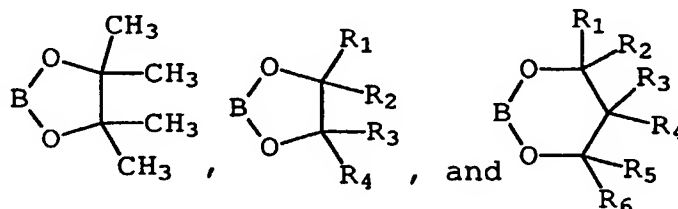


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wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; (PY_7P) is $R_{18}R_{19}\text{P}-Y_7-\text{PR}_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain
15 containing 1 to 12 carbons.

-11-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(\text{PY}_7\text{P})(\text{P}(\text{Y}_4)(\text{Y}_5)(\text{Y}_6))\text{Ir}(\text{BY})_3$ wherein BY is a boron moiety selected from the group consisting of



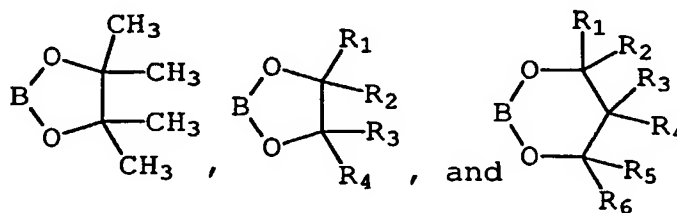
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- 107 -

wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

-12-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(PY_7P)(P(R_{14})(R_{15})(R_{16}))Ir(BY)_3$ wherein BY is a boron moiety selected from the group consisting of



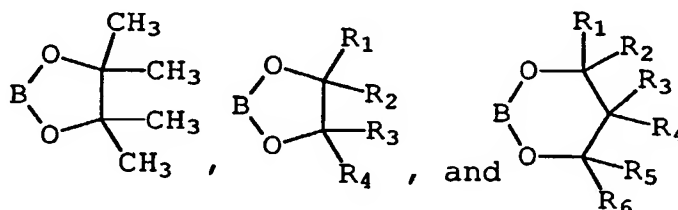
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wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic

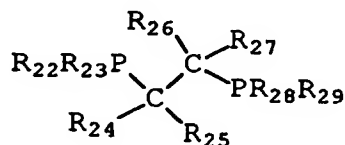
structure; R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each
 5 selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

-13-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $\{(P^{\wedge}P)Ir(BY)_3\}_2(\mu_2-(P^{\wedge}P))$ wherein BY is a boron moiety selected from the group consisting of



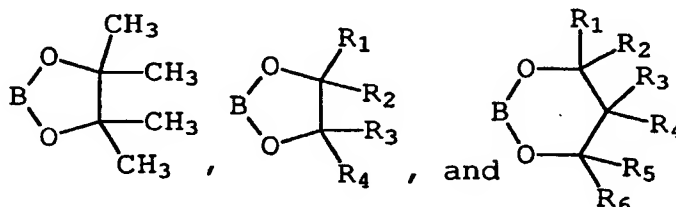
5 wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic
 10 structure; and wherein $(P^{\wedge}P)$ is of the formula



wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

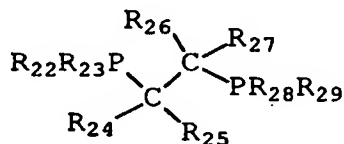
-14-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(P^{\sim}P)(P(Y_4)(Y_5)(Y_6))Ir(BY)_3$ wherein BY is a boron moiety selected from the group consisting of



5

wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and wherein $(P^{\sim}P)$ is of the formula

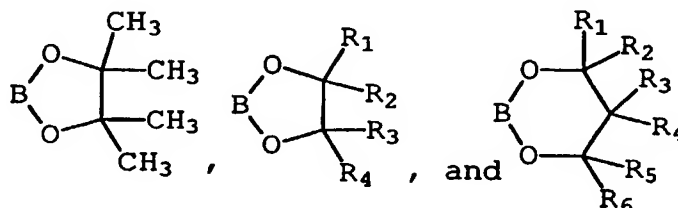


wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

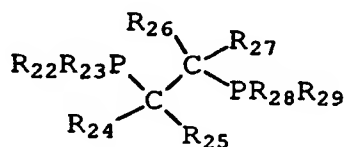
-15-

- 110 -

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(P^{\sim}P)(P(R_{14})(R_{15})(R_{16}))Ir(BY)_3$ wherein BY is a boron moiety selected from the group consisting of



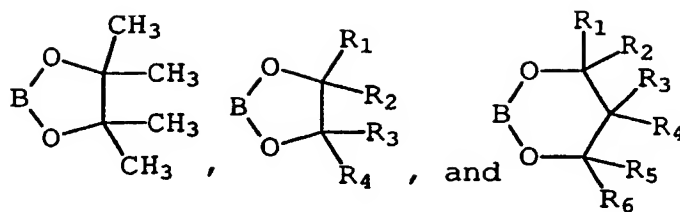
- 5 wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; and wherein $(P^{\sim}P)$ is of the formula



- 15 wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

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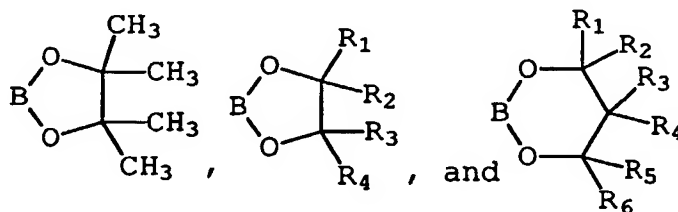
The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(PY_7P)Ir(BY)_3$ wherein BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

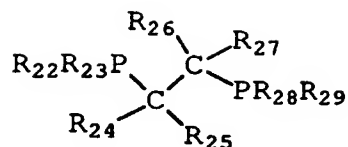
-17-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(P^*P)Ir(BY)_3$ wherein BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and wherein (P^*P) is of the formula

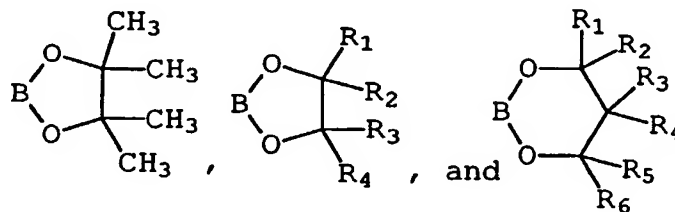
- 112 -



wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

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The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(P(Y_4)(Y_5)(Y_6))_4Ir(BY)$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide
 5 $(-O(R_{11}))$, and amide $(-N(R_{12})(R_{13}))$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and BY is a boron moiety
 10 selected from the group consisting of



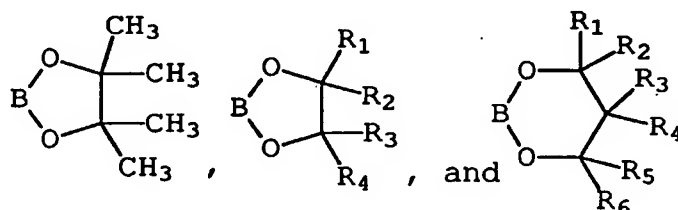
wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl
 15 containing 1 to 8 carbons, and a carbon in a cyclic structure.

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The catalytic composition of Claim 1 or 2

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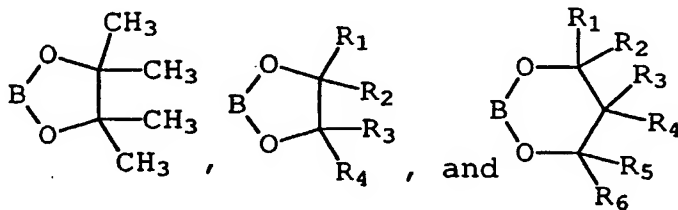
wherein the iridium complex is $(P(R_{14})(R_{15})(R_{16}))_4Ir(BY)$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; and BY is a
 5 boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl
 10 containing 1 to 8 carbons, and a carbon in a cyclic structure.

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The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(PY_7P)(P(Y_4)(Y_5)(Y_6))_2Ir(BY)$ wherein BY is a boron moiety selected from the group consisting of



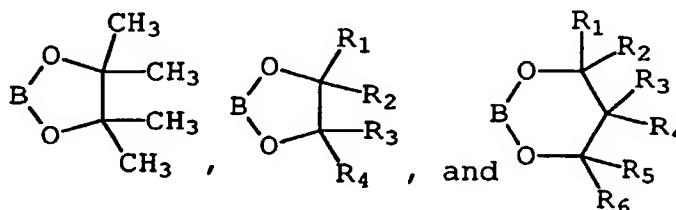
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wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic
 10 structure; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl,

alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

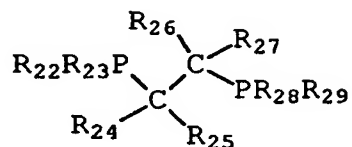
-21-

The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(P^{\sim}P)(P(Y_4)(Y_5)(Y_6))_2Ir(BY)$ wherein BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a

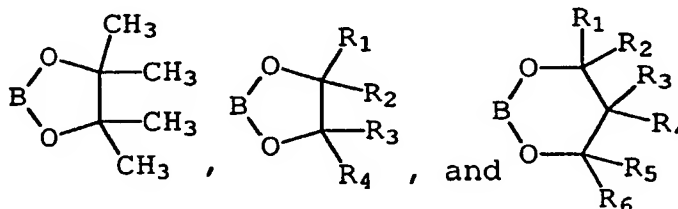
carbon in a cyclic structure; and wherein (P⁻P) is of the formula



wherein R₂₂, R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈, and R₂₉ are each
 5 selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

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The catalytic composition of Claim 1 or 2 wherein the iridium complex is (PY₇P) (P(R₁₄) (R₁₅) (R₁₆))₂Ir(BY) wherein BY is a boron moiety selected from the group consisting of



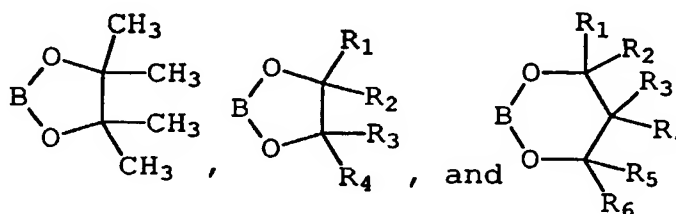
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wherein R₁, R₂, R₃, R₄, R₅, and R₆ are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; R₁₄, R₁₅, and R₁₆ are each selected from the
 10 group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; (PY₇P) is R₁₈R₁₉P-Y₇-PR₂₀R₂₁ wherein R₁₈, R₁₉, R₂₀, and R₂₁ are each selected from the group consisting of hydrogen, linear
 15 alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y₇ is a chain containing 1 to 12

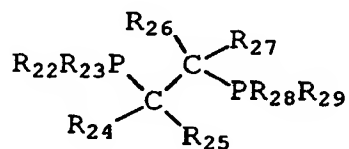
carbons.

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The catalytic composition of Claim 1 or 2 wherein the iridium complex is $(P^{\sim}P)(P(R_{14})(R_{15})(R_{16}))_2Ir(BY)$ wherein BY is a boron moiety selected from the group consisting of



- 5 wherein $R_1, R_2, R_3, R_4, R_5,$ and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; $R_{14}, R_{15},$ and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; and wherein
- 10 $(P^{\sim}P)$ is of the formula



- 15 wherein $R_{22}, R_{23}, R_{24}, R_{25}, R_{26}, R_{27}, R_{28},$ and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

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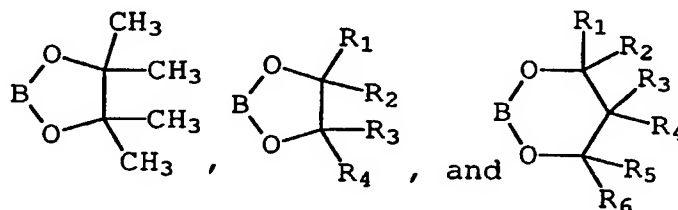
The catalytic composition of Claim 1 or 2 wherein the iridium complex is selected from the group consisting of $(Cp^*)Ir(H)_2(Me_3P),$

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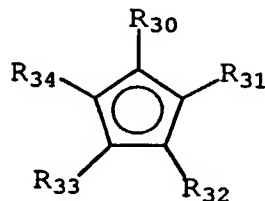
$(Cp^*)Ir(H)(BPin)(Me_3P)$, $(CP^*)Ir(H)(C_6H_5)(Me_3P)$,
 $(Ind)_3Ir(COD)$, $(MesH)Ir(BPin)(B(OR)_2)$,
 $((R_1)_3P)_3Ir(B(OR)_2)_3$, $(R_1)_2P)_2Ir(BPin)_3$,
 $[((R_1)_2P)_3Ir((R_2O)_2B)_3]_2$, $((R_1)_3P)_4Ir(BPin)$,
5 $((R_1)_2P)_2Ir(BPin)_3$, $(MesH)Ir(BPin)_3$, $IrCl(COD)$, and
 $[IrCl(COD)]_2$, wherein CP^* is 1,2,3,4,5-
methylcyclopentadienyl, BPin is pinacolborane, Me is
methyl, H is hydrogen, P is phosphorus, Ind is
indenyl, COD is 1,5-cyclooctadiene, MesH is
10 mesitylene, and wherein R, R_1 , and R_2 are each selected
from the group consisting of hydrogen, linear or
branched alkyl containing 1 to 8 carbons, aryl, and a
carbon in a cyclic structure.

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The catalytic composition of Claim 1 or 2 wherein the rhodium complex is $(Cp')(P(Y_4)(Y_5)(Y_6))Rh(H)_n(BY)_{2-n}$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide $(-O(R_{11}))$, and amide $(-N(R_{12})(R_{13}))$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; n is 0 or 1; BY is a boron moiety selected from the group consisting of



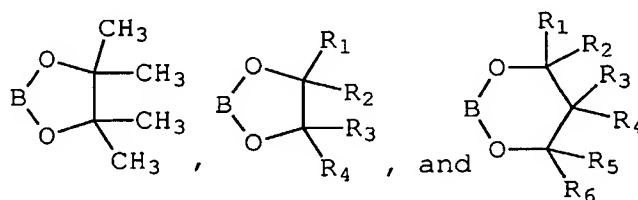
wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and Cp' is of the formula



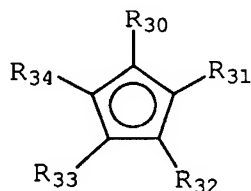
wherein R_{30} , R_{31} , R_{32} , R_{33} , and R_{34} are each selected from the group consisting of hydrogen, alkyl chains, carbocyclic rings, and aryl groups.

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The catalytic composition of Claim 1 or 2 wherein the rhodium complex is $(Cp')(P(R_{14}(R_{15})(R_{16}))Rh(H)_n(BY)_{2-n}$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; n is 0 or 1; BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and Cp' is of the formula



wherein R_{30} , R_{31} , R_{32} , R_{33} , and R_{34} are each selected from the group consisting of hydrogen, alkyl chains, carbocyclic rings, and aryl groups.

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The catalytic composition of Claim 1 or 2 wherein the rhodium complex is selected from the group consisting of $(Cp^*)Rh(H)_2(Me_3P)$, $(Cp^*)Rh(H)(BPin)(Me_3P)$, $(Cp^*)Rh(H)(C_6H_5)(Me_3P)$, and

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(Cp*)Rh(hexamethylbenzene), wherein CP* is 1,2,3,4,5-methylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, and P is phosphorus.

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A process for producing a ring-substituted arene borane which comprises:

reacting a ring-substituted arene with an HB
5 organic compound in the presence of a catalytically effective amount of an iridium or rhodium complex with three or substituents, excluding hydrogen, bonded to the iridium or rhodium, to form the ring-substituted arene borane.

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A process for producing a ring-substituted arene borane which comprises:

reacting a ring-substituted arene with an HB
organic compound in the presence of a catalytically
5 effective amount of an iridium or rhodium complex with three or substituents, excluding hydrogen, bonded to the iridium or rhodium and a phosphorus organic ligand, in a molar ratio of complex to ligand between about 1 to 3 and 1 to 1, wherein the ligand is at
10 least in part bonded to the iridium or rhodium, to form the ring-substituted arene borane.

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The process of Claim 29 wherein the phosphorus organic ligand is selected from the group consisting of trimethyl phosphine (PMe₃), 1,2-

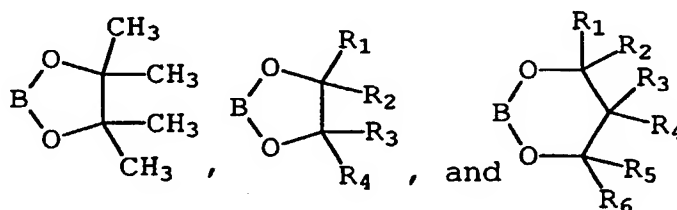
- 121 -

bis(dimethylphosphino)ethane (dmpe), and 1,2-bis(diphenylphosphino)ethane (dppe).

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The process of Claim 29 or 30 wherein the iridium complex is $(ArH)Ir(BY)_3$ wherein ArH is selected from the group consisting of aromatic, heteroaromatic, polyaromatic, and heteropolyaromatic hydrocarbon; and

5 BY is a boron moiety of the formula

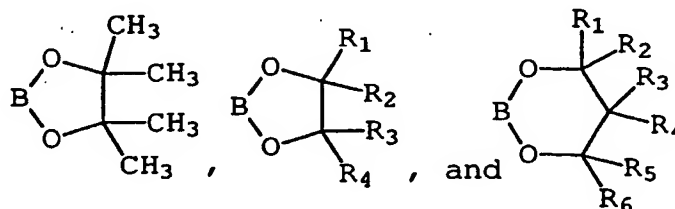


wherein R₁, R₂, R₃, R₄, R₅, and R₆ are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl

10 containing 1 to 8 carbons, and a carbon in a cyclic structure.

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The process of Claim 29 or 30 wherein the iridium complex is $(MesH)Ir(BY)_3$ wherein MesH is mesitylene; and BY is a boron moiety selected from the group consisting of



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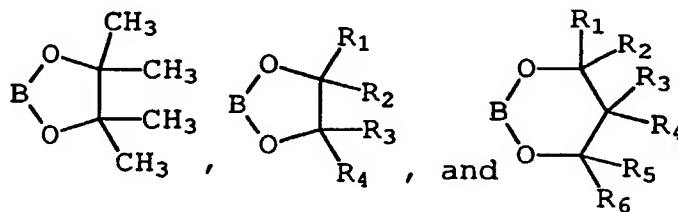
wherein R₁, R₂, R₃, R₄, R₅, and R₆ are each selected

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from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

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The process of Claim 29 or 30 wherein the iridium complex is $(P(Y_4)(Y_5)(Y_6))_3Ir(H)_n(BY)_{3-n}$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide
 5 $(-O(R_{11}))$, and amide $(-N(R_{12})(R_{13}))$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; n is 0, 1, or 2; and BY is a
 10 boron moiety selected from the group consisting of

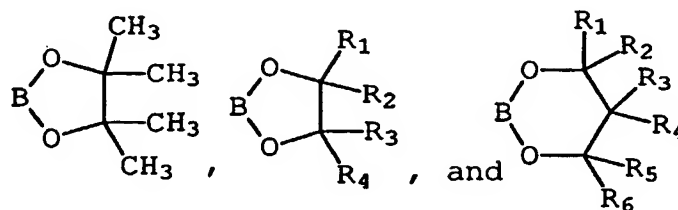


wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl
 15 containing 1 to 8 carbons, and a carbon in a cyclic structure.

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The process of Claim 29 or 30 wherein the iridium complex is $(P(R_{14})(R_{15})(R_{16}))_3Ir(H)_n(BY)_{3-n}$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl, branched

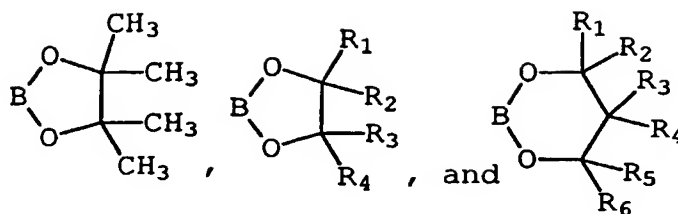
alkyl, and a carbon in a cyclic structure; n is 0, 1, or 2; and BY is a boron moiety selected from the group consisting of



- 5 wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

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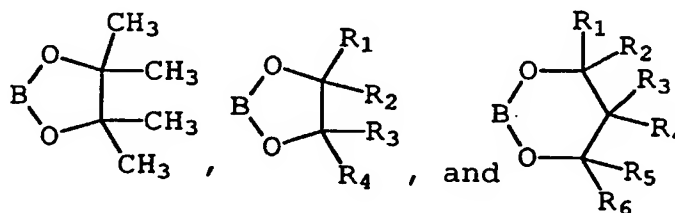
- The process of Claim 29 or 30 wherein the iridium complex is $(P(Y_4)(Y_5)(Y_6))_3Ir(H)(R_{17})(BY)$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide
 5 $(-O(R_{11}))$, and amide $(-N(R_{12})(R_{13}))$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; R_{17} is selected from the group
 10 consisting of a linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure; and BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

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The process of Claim 29 or 30 wherein the iridium complex is $(P(R_{14})(R_{15})(R_{16}))_3Ir(H)(R_{17})(BY)$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; R_{17} is selected from the group consisting of a linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, aryl, and a carbon in a cyclic structure; and BY is a boron moiety selected from the group consisting of

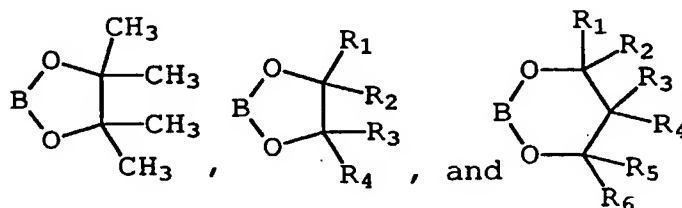


wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

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The process of Claim 29 or 30 wherein the iridium complex is $\{(\text{PY}_7\text{P})\text{Ir}(\text{BY})_3\}_2(\mu_2-(\text{PY}_7\text{P}))$ wherein BY is a boron moiety selected from the group consisting of

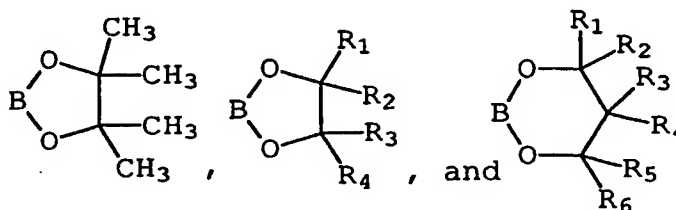


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wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; (PY_7P) is $R_{18}R_{19}\text{P}-Y_7-\text{PR}_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain
10
15 containing 1 to 12 carbons.

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The process of Claim 29 or 30 wherein the iridium complex is $(\text{PY}_7\text{P})(\text{P}(\text{Y}_4)(\text{Y}_5)(\text{Y}_6))\text{Ir}(\text{BY})_3$ wherein BY is a boron moiety selected from the group consisting of



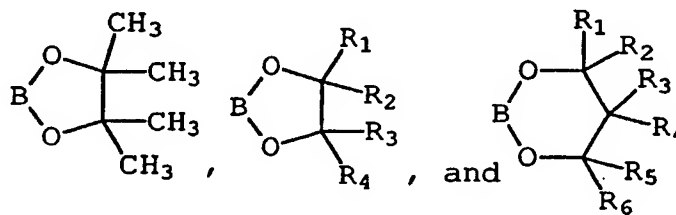
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- 126 -

wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

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The process of Claim 29 or 30 wherein the iridium complex is $(PY_7P)(P(R_{14})(R_{15})(R_{16}))Ir(BY)_3$ wherein BY is a boron moiety selected from the group consisting of



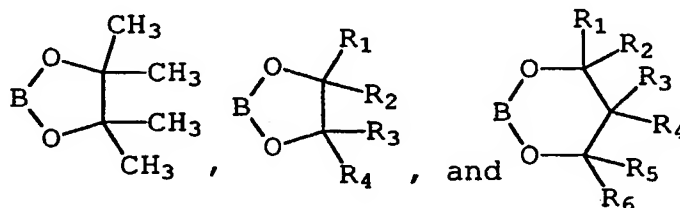
wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic

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structure; R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each
 5 selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

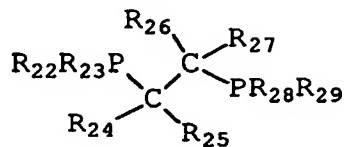
-40-

The process of Claim 29 or 30 wherein the iridium complex is $\{(P^{\wedge}P)Ir(BY)_3\}_2(\mu_2-(P^{\wedge}P))$ wherein BY is a boron moiety selected from the group consisting of



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wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic
 10 structure; and wherein $(P^{\wedge}P)$ is of the formula

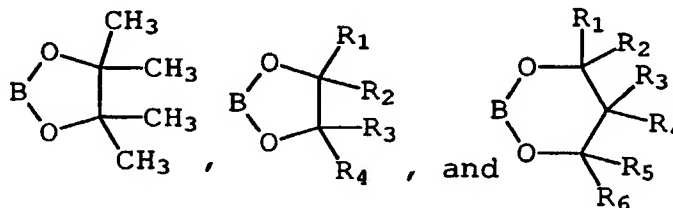


wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

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The process of Claim 29 or 30 wherein the iridium complex is $(P^{\sim}P)(P(Y_4)(Y_5)(Y_6))Ir(BY)_3$ wherein BY is a boron moiety selected from the group consisting of

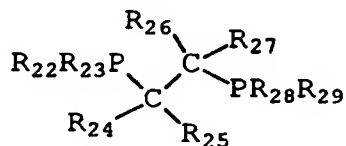


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wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and wherein $(P^{\sim}P)$ is of the formula

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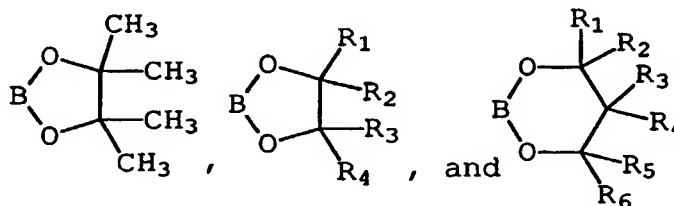
wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

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-42-

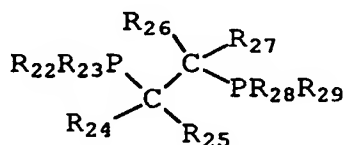
- 129 -

The process of Claim 29 or 30 wherein the iridium complex is $(P^{\sim}P)(P(R_{14})(R_{15})(R_{16}))Ir(BY)_3$ wherein BY is a boron moiety selected from the group consisting of



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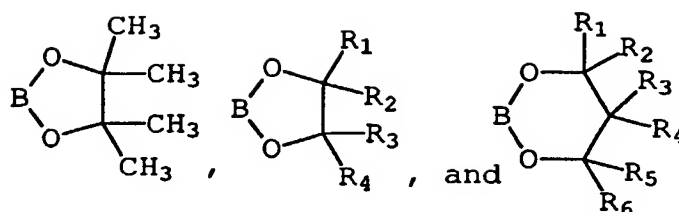
wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; and wherein $(P^{\sim}P)$ is of the formula



15 wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

-43-

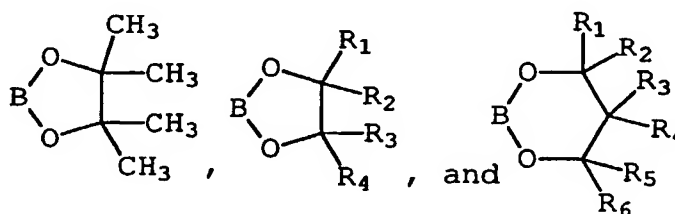
The process of Claim 29 or 30 wherein the iridium complex is $(PY_7P)Ir(BY)_3$ wherein BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and (PY₇P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

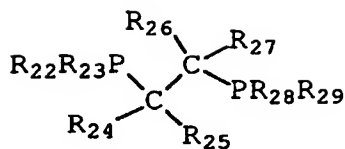
-44-

The process of Claim 29 or 30 wherein the iridium complex is $(P^{\wedge}P)Ir(BY)_3$ wherein BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and wherein $(P^{\wedge}P)$ is of the formula

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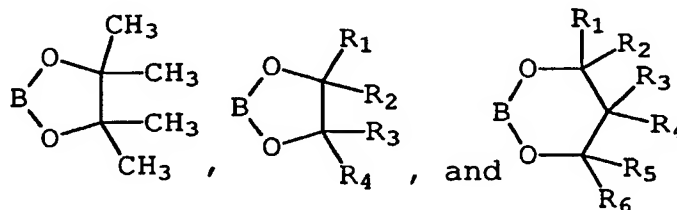


wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

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-45-

The process of Claim 29 or 30 wherein the iridium complex is $(P(Y_4)(Y_5)(Y_6))_4Ir(BY)$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and BY is a boron moiety selected from the group consisting of

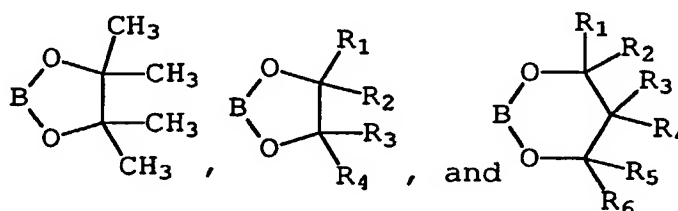


wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure.

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The process of Claim 29 or 30 wherein the

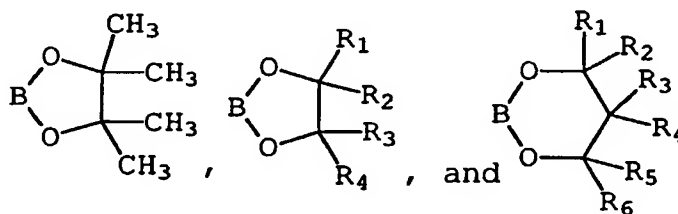
iridium complex is $(P(R_{14})(R_{15})(R_{16}))_4Ir(BY)$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; and BY is a boron moiety
 5 selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl
 10 containing 1 to 8 carbons, and a carbon in a cyclic structure.

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The process of Claim 29 or 30 wherein the iridium complex is $(PY_7P)(P(Y_4)(Y_5)(Y_6))_2Ir(BY)$ wherein BY is a boron moiety selected from the group consisting of

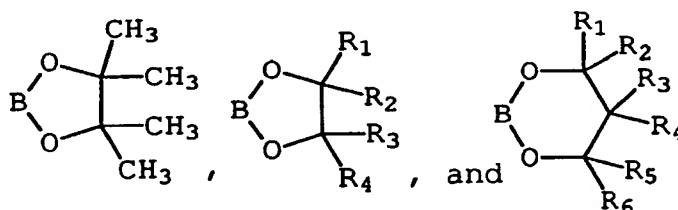


5 wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; Y_4 , Y_5 , and Y_6 are each selected from the
 10 group consisting of hydrogen, halide, alkyl, aryl,

alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and (PY_7P) is $R_{18}R_{19}P-Y_7-PR_{20}R_{21}$ wherein R_{18} , R_{19} , R_{20} , and R_{21} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y_7 is a chain containing 1 to 12 carbons.

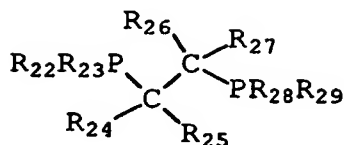
-48-

The process of Claim 29 or 30 wherein the iridium complex is $(P^{\sim}P)(P(Y_4)(Y_5)(Y_6))_2Ir(BY)$ wherein BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a

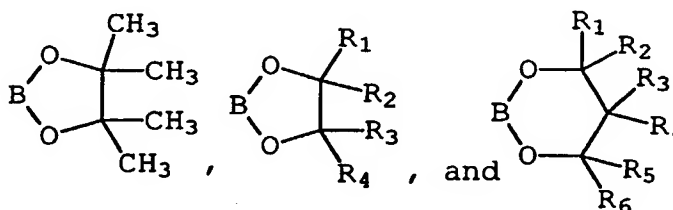
carbon in a cyclic structure; and wherein (P[~]P) is of the formula



wherein R₂₂, R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈, and R₂₉ are each
5 selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

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The process of Claim 29 or 30 wherein the iridium complex is (PY₇P)(P(R₁₄)(R₁₅)(R₁₆))₂Ir(BY) wherein BY is a boron moiety selected from the group consisting of



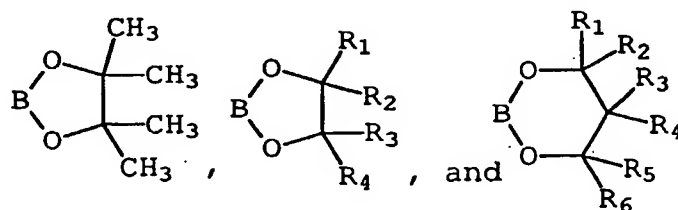
5

wherein R₁, R₂, R₃, R₄, R₅, and R₆ are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; R₁₄, R₁₅, and R₁₆ are each selected from the
10 group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; (PY₇P) is R₁₈R₁₉P-Y₇-PR₂₀R₂₁ wherein R₁₈, R₁₉, R₂₀, and R₂₁ are each selected from the group consisting of hydrogen, linear
15 alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure, and Y₇ is a chain containing 1 to 12

carbons.

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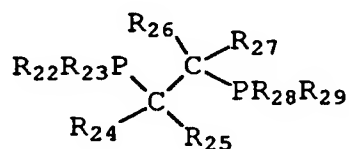
The process of Claim 29 or 30 wherein the iridium complex is $(P^{\sim}P)(P(R_{14})(R_{15})(R_{16}))_2Ir(BY)$ wherein BY is a boron moiety selected from the group consisting of



5

wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; and wherein $(P^{\sim}P)$ is of the formula

10



15 wherein R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , and R_{29} are each selected from the group consisting of alkyl chains, carbocyclic rings, and aryl groups.

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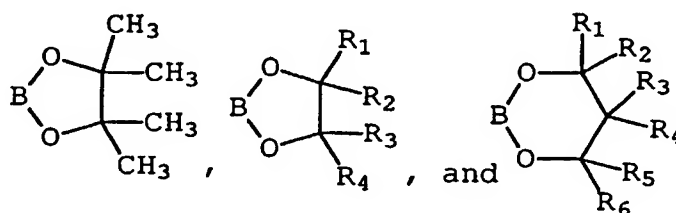
The process of Claim 29 or 30 wherein the iridium complex is selected from the group consisting of $(Cp^*)Ir(H)_2(Me_3P)$, $(Cp^*)Ir(H)(BPin)(Me_3P)$,

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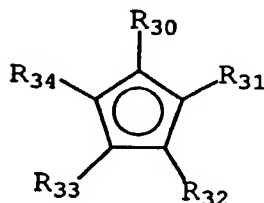
$(CP^*) Ir(H)(C_6H_5)(Me_3P)$, $(Ind) Ir(COD)$,
 $(MesH) Ir(BPin)(B(OR)_2)$, $((R_1)_3P)_3 Ir(B(OR_2)_2)_3$,
 $(R_1)_2P)_2 Ir(BPin)_3$, $[((R_1)_2P)_3 Ir((R_2O)_2B)_3]_2$,
 $((R_1)_3P)_4 Ir(BPin)$, $((R_1)_2P)_2 Ir(BPin)_3$, $(MesH) Ir(BPin)_3$,
5 $IrCl(COD)$, and $[IrCl(COD)]_2$, wherein CP^* is 1,2,3,4,5-
methylcyclopentadienyl, BPin is pinacolborane, Me is
methyl, H is hydrogen, P is phosphorus, Ind is
indenyl, COD is 1,5-cyclooctadiene, MesH is
mesitylene, and wherein R, R_1 , and R_2 are each selected
10 from the group consisting of hydrogen, linear or
branched alkyl containing 1 to 8 carbons, aryl, and a
carbon in a cyclic structure.

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The process of Claim 29 or 30 wherein the rhodium complex is $(\text{Cp}')(\text{P}(\text{Y}_4)(\text{Y}_5)(\text{Y}_6))\text{Rh}(\text{H})_n(\text{BY})_{2-n}$ wherein Y_4 , Y_5 , and Y_6 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide
 5 $(-\text{O}(\text{R}_{11}))$, and amide $(-\text{N}(\text{R}_{12})(\text{R}_{13}))$ wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; n is 0 or 1; BY is a boron
 10 moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl
 15 containing 1 to 8 carbons, and a carbon in a cyclic structure; and Cp' is of the formula

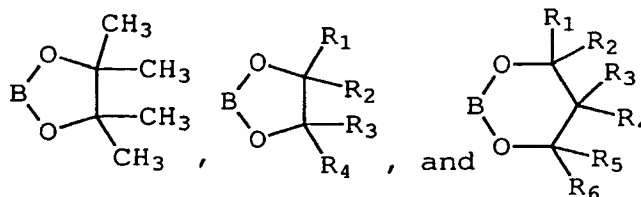


wherein R_{30} , R_{31} , R_{32} , R_{33} , and R_{34} are each selected from the group consisting of hydrogen, alkyl chains, carbocyclic rings, and aryl groups.
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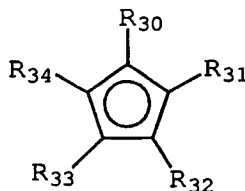
-53-

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The process of Claim 29 or 30 wherein the rhodium complex is $(Cp')(P(R_{14}(R_{15})(R_{16}))Rh(H)_n(BY)_{2-n}$ wherein R_{14} , R_{15} , and R_{16} are each selected from the group consisting of hydrogen, linear alkyl, branched alkyl, and a carbon in a cyclic structure; n is 0 or 1; BY is a boron moiety selected from the group consisting of



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; and Cp' is of the formula



wherein R_{30} , R_{31} , R_{32} , R_{33} , and R_{34} are each selected from the group consisting of hydrogen, alkyl chains, carbocyclic rings, and aryl groups.

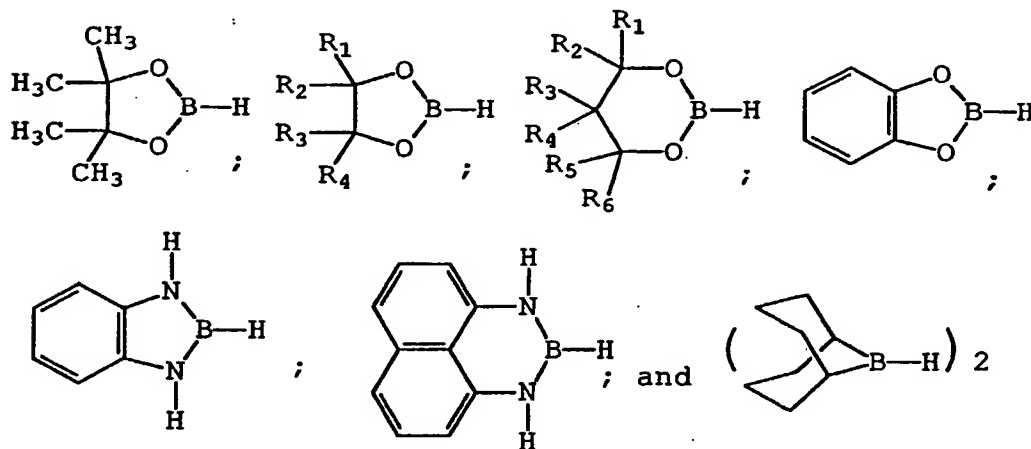
-54-

The process of Claim 29 or 30 wherein the rhodium complex is selected from the group consisting of $(Cp^*)Rh(H)_2(Me_3P)$, $(Cp^*)Rh(H)(BPin)(Me_3P)$, $(Cp^*)Rh(H)(C_6H_5)(Me_3P)$, and $(Cp^*)Rh(\text{hexamethylbenzene})$, wherein CP^* is 1,2,3,4,5-methylcyclopentadienyl, $BPin$

methylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, and P is phosphorus.

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The process of Claim 29 or 30 wherein the HB organic compound is selected from the group consisting of $B(H)(Y_{11})(Y_{12})$ wherein Y_{11} and Y_{12} are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide ($-O(R_{11})$), and amide ($-N(R_{12})(R_{13})$) wherein R_{11} , R_{12} , and R_{13} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbons, and a carbon in a cyclic structure; $B(H)(Y_{13}-Y_{14}-Y_{15})$ wherein Y_{13} and Y_{15} are each selected from the group consisting of alkyl, aryl, oxygen, and nitrogen and Y_{14} is a chain containing 1 to 12 carbon atoms;

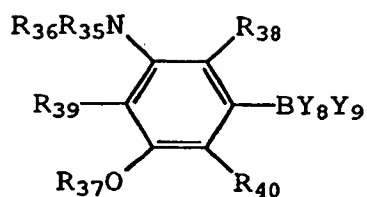


15 .

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A ring-substituted arene borane of the formula

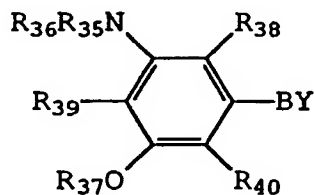
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wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element
 5 wherein the element is bound to boron; R_{35} , R_{36} , and R_{37} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing
 10 moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and R_{38} , R_{39} , and R_{40} are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide,
 15 amide, and a group containing any other element which is bound to the aromatic ring.

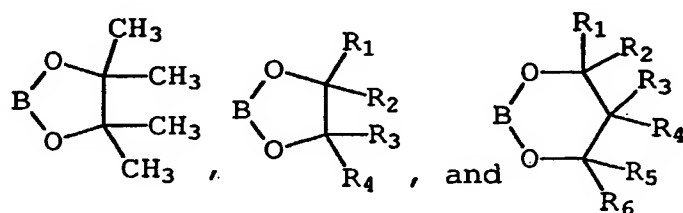
-57-

A ring-substituted arene borane of the formula



wherein R_{35} , R_{36} , and R_{37} are each selected from the
 5 group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure,

a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and R_{38} , R_{39} , and R_{40} are each
 5 selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element which is bound to the aromatic ring; and BY is a boron moiety selected from the group consisting of

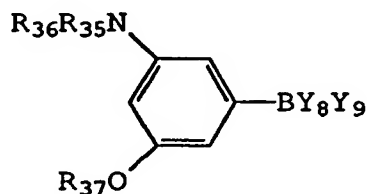


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wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, and carbon
 15 within a cyclic structure.

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A ring-substituted arene borane of the formula

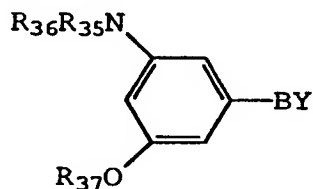


wherein Y_8 and Y_9 are each selected from the group
 5 consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron; and R_{35} , R_{36} , and

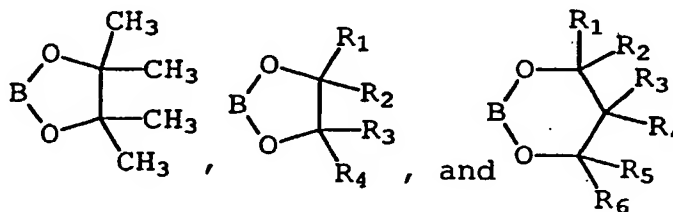
R_{37} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group.

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A ring-substituted arene borane of the formula



wherein R_{35} , R_{36} , and R_{37} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and BY is a boron moiety selected from the group consisting of

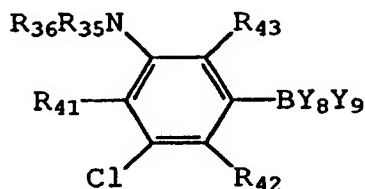


wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each selected from the group consisting of hydrogen, linear alkyl

containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, and carbon within a cyclic structure.

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A ring-substituted arene borane of the formula

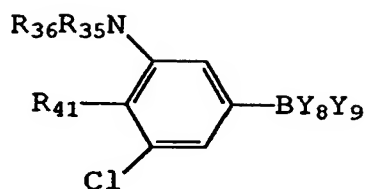


wherein Y_8 and Y_9 are each selected from the group
 5 consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron; R_{35} and R_{36} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched
 10 alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and R_{41} , R_{42} , and
 15 R_{43} are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element which is bound to the aromatic ring.

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A ring-substituted arene borane of the formula

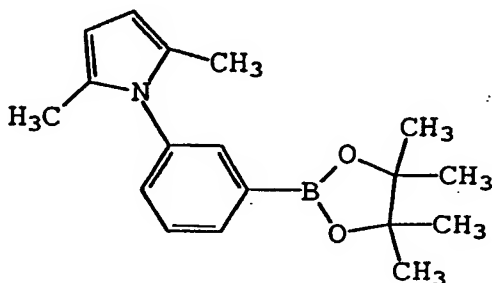
- 145 -



wherein Y_8 and Y_9 are each selected from the group consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element
 5 wherein the element is bound to boron; R_{35} and R_{36} are each selected from the group consisting of hydrogen, linear alkyl containing 1 to 8 carbon atoms, branched alkyl containing 1 to 8 carbon atoms, aryl, carbon within a cyclic structure, a silicon containing moiety
 10 wherein the silicon is bound to a nitrogen or oxygen which is bound to the aromatic ring, amine protecting group, and alcohol protecting group; and R_{41} is selected from the group consisting of halide, alkyl, aryl, alkoxide, amide, and a group containing any
 15 other element except hydrogen which is bound to the aromatic ring.

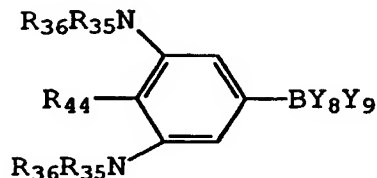
-62-

A ring-substituted arene borane of the formula



-63-

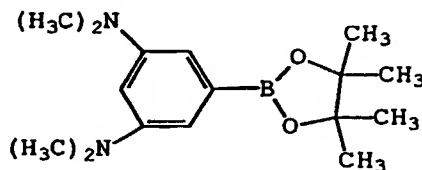
A ring-substituted arene borane of the formula



wherein Y_8 and Y_9 are each selected from the group
 5 consisting of hydrogen, halide, alkyl, aryl, alkoxide,
 amide, and a group containing any other element
 wherein the element is bound to boron; R_{35} and R_{36} are
 each selected from the group consisting of hydrogen,
 linear alkyl containing 1 to 8 carbon atoms, branched
 10 alkyl containing 1 to 8 carbon atoms, aryl, carbon
 within a cyclic structure, a silicon containing moiety
 wherein the silicon is bound to a nitrogen or oxygen
 which is bound to the aromatic ring, amine protecting
 group, and alcohol protecting group; and R_{44} is
 15 selected from the group consisting of alkoxide, amide,
 and a group containing any other element which is
 bound to the aromatic ring except for hydrogen or
 carbon.

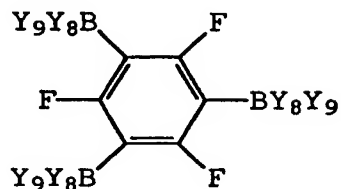
-64-

A ring-substituted arene borane of the formula



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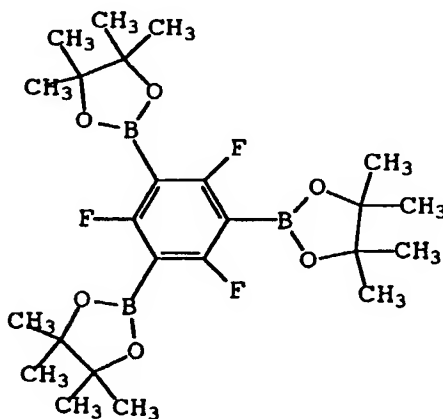
A ring-substituted arene borane of the formula



wherein Y_8 and Y_9 are each selected from the group
 5 consisting of hydrogen, halide, alkyl, aryl, alkoxide, amide, and a group containing any other element wherein the element is bound to boron.

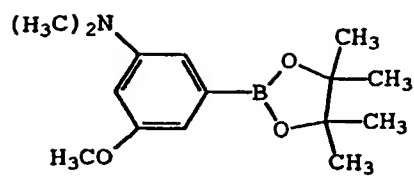
-66-

A ring-substituted arene borane of the formula



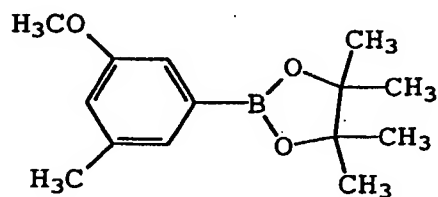
-67-

A ring-substituted arene borane of the formula

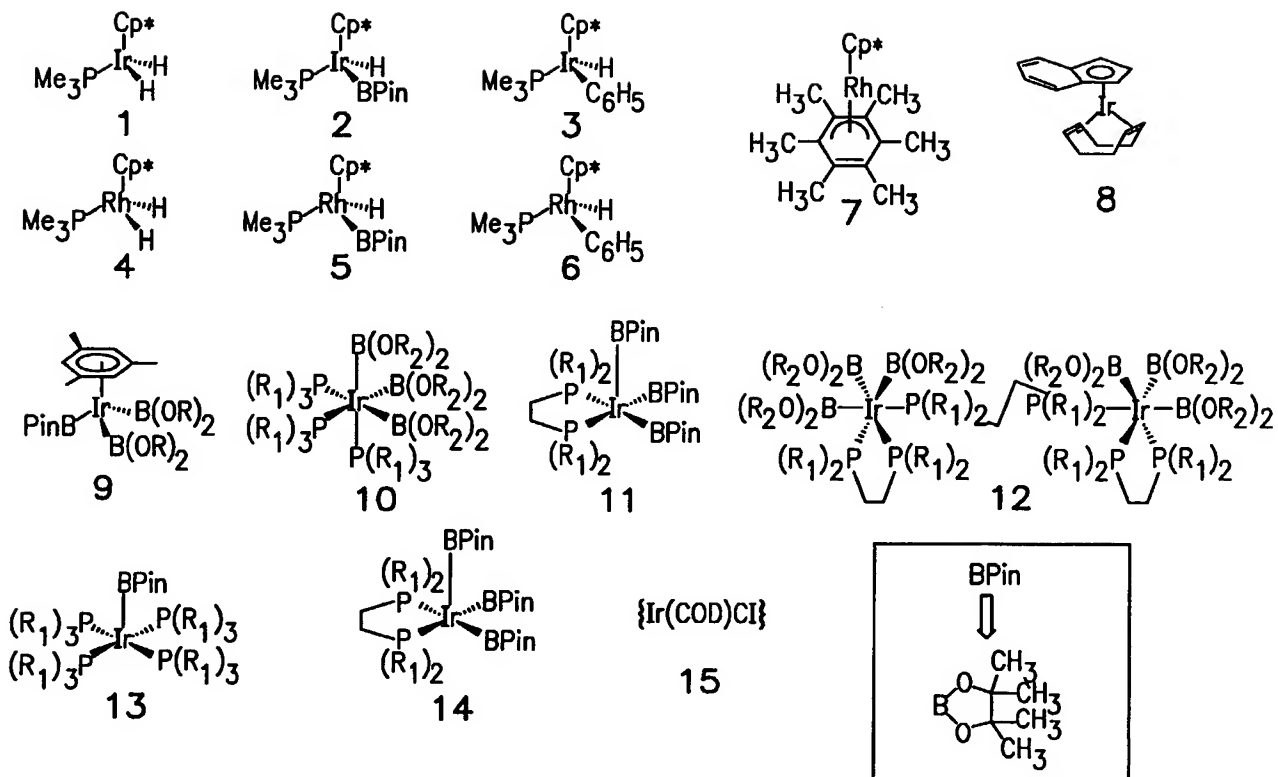


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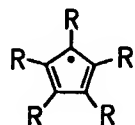
A ring-substituted arene borane of the formula



1/2



Cyclopentadienyl

Cp* \rightarrow R=CH₃

Indenyl

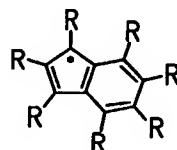
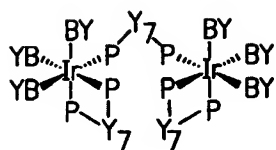
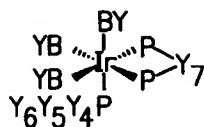
Ind \rightarrow R=H

FIG. 1

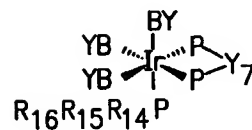
2/2



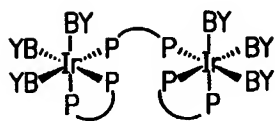
16



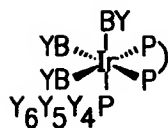
17



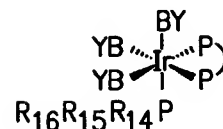
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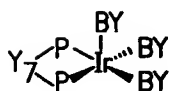
19



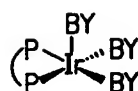
21



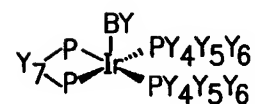
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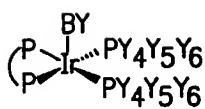
22



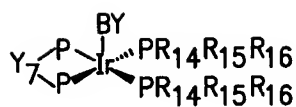
23



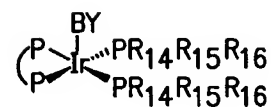
24



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FIG. 2

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
23 January 2003 (23.01.2003)

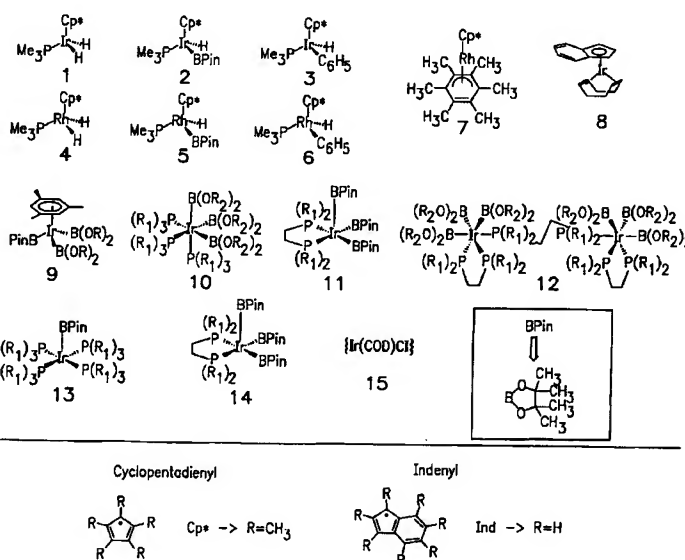
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- (21) International Application Number: PCT/US02/23302
- (22) International Filing Date: 13 July 2002 (13.07.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/305,107 13 July 2001 (13.07.2001) US
- (71) Applicant: **MICHIGAN STATE UNIVERSITY**
[US/US]; 238 Administration Building, East Lansing, MI 48824 (US).
- (72) Inventor: **SMITH, Milton, R., III**; 238 Oxford Road, East Lansing, MI 48823 (US).
- (74) Agent: **MCLEOD, Ian, C.**; McLeods & Moyne, P.C., 2190 Commons Parkway, Okemos, MI 48864 (US).
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- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- (88) Date of publication of the international search report:
3 April 2003

[Continued on next page]

(54) Title: CATALYTIC BORONATE ESTER SYNTHESIS FROM BORON REAGENTS AND HYDROCARBONS



(57) Abstract: A process for producing a ring-substituted arene borane which comprises reacting a ring-substituted arene with an HB organic compound in the presence of a catalytically effective amount of an iridium or rhodium complex with three or more substituents, excluding hydrogen, bonded to the iridium or rhodium and a phosphorus organic ligand, which is at least in part bonded to the iridium or rhodium, to form the ring-substituted arene borane. Also provided are catalytic compounds for catalyzing the process comprising an iridium or rhodium complex with three or substituents, excluding hydrogen, bonded to the iridium or rhodium and optionally, a phosphorus organic ligand, which is at least in part bonded to the iridium or rhodium.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/23302

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/152, 155, 162, 166, 167, 172; 556/7, 21, 136, 137; 568/1, 6, 630, 631; 548/110; 564/305

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS structure search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	COTTON, F.A. et al., "Advanced Inorganic Chemistry", 4th ed., 1980, pp. 940-941.	1, 2, 3
X	US 5,260,491 A (WINK et al.) 09 November 1993, col. 7, l. 35-50.	1-3
X	US 4,906,415 A (LUFT et al.) 06 March 1990, col. 4, l. 10-18.	1-3
X	US 5,334,791 A (CAVELL et al.) 02 August 1994, col. 1, l. 24, 57; col. 2, l. 32-35; col. 3, l. 68; col. 5, l. 21-23; col. 19, table 1	1-3
X	US 5,488,153 A (BAKER et al.) 30 January 1996, col. 9, table 3	1-3

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

•	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
12 NOVEMBER 2002	18 DEC 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer JAMES PASTERCZYK
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/23302

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,498,584 A (PUCKETTE) 12 March 1996, col. 3, l. 66 to col. 4, l. 35	1-3
X	US 5,574,171 A (AYERS et al.) 12 November 1996, col. 5, l. 10-16	1
X	US 4,733,007 A (ANDRADE et al.) 22 March 1988, col. 2, l. 33-34	1, 2
X,P	US 6,323,353 A (SUMI et al.) 27 November 2001, col. 17, l. 13-45	1-3
X	US 4,605,781 A (TAU) 12 August 1986, col. 10-11, table VI	1-3
X	US 4,446,074 A (JAMERSON et al.) 01 May 1984, col. 15, l. 25-29	1-3
X	US 4,201,714 A (HUGHES) 06 May 1980, col. 10, l. 6-19	1-3
X	US 5,789,609 A (TAMAO et al.) 04 August 1998, col. 5, l. 20-30, col. 6, l. 1-9	1-2
X	US 5,563,308 A (SPINDLER et al.) 08 October 1996, col. 10, l. 34-35	1
X,P	US 6,399,804 B2 (WALTER et al.) 04 June 2002, col. 2, l. 58-59	1
X	US 4,668,809 A (OSWALD et al.) 26 May 1987, col. 55-60, tables 4-6	1-3
X	CLEGG, W. et al., J. Chem. Soc., Dalton Trans., 1998, pp. 301-309, especially figs 1-4	1-27
X	CLEARY, B. et al., Organometallics, vol. 14, no. 10, pp. 4525-4534, 1995, see reaction schemes 1, 5, 6, 7 and 17	1-27
X	IVERSON, C. et al., J. Am. Chem. Soc., vol. 121, no. 33, pp. 7696-7697, 1999, see reaction schemes 3 and 4	1-27
X	CHO, J.-Y. et al., J. Am. Chem. Soc., vol. 122, no. 51, pp. 12868-12869, 2000, see second paragraph of first column of first page	1-27
X	DAI, C. et al., Can. J. Chem., vol. 74, 1996, pp. 2026-2031, see reaction scheme 3, figure 1	1-27
X	WESTCOTT, S. et al., Can. J. Chem., vol. 71, 1993, pp. 930-936, see reaction schemes 1-3, figure 1	1-27

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/23302

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WESTCOTT, S. et al., J. Chem. Soc., Chem. Commun., 1991, pp. 304-305, see figures 1-3	1-27
X	MARDER, T. et al., J. Chem. Soc., Chem. Commun., 1997, pp. 53-54, see bottom left of first page	1-27
X	NGUYEN, P. et al., Inorg. Chem., vol. 33, no. 21, pp. 4623-4624, 1994, see top right of first page	1-27
X	NGUYEN, P. et al., J. Am. Chem. Soc., vol. 115, no. 20, pp. 9329-9330, 1993, see figure 1	1-27
X	BAKER, R.T. et al., J. Am. Chem. Soc., vol. 115, no. 10, pp. 4367-4368, 1993, see figure 1	1-27
X	BURGESS, K. et al., J. Am. Chem. Soc., vol. 114, no. 24, pp. 9350-9359, 1992, see scheme 1, figure 1, tables II and IV	1-27
X	WESTCOTT, S. et al., Inorg. Chem., vol. 32, no. 10, pp. 2175-2182, 1993, see scheme VI	1-27
X	DAI, C. et al., Inorg. Chem., vol. 36, no. 3, pp. 272-273, 1997, see figure 1	1-27
X	KNORR, J. et al., Organometallics, vol. 9, no. 12, pp. 3008-3010, see figure 1, first reaction of p. 3009	1-27

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/23302

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (7):

B01J 31/00; C07D 231/00, 233/00, 235/00, 249/00, 261/00, 263/00, 271/00, 273/00, 275/00, 277/00, 283/00, 285/00, 291/00, 293/00, 413/00, 417/00, 419/00, 421/00, 498/00, 513/00, 515/00, 517/00; C07F 15/00, 17/02, 5/02, 9/02; C07C 211/00, 41/00, 43/02, 43/20

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

502/152, 155, 162, 166, 167, 172; 556/7, 21, 136, 137; 568/1, 6, 630, 631; 548/110; 564/305

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-55, drawn to catalysts and methods of using them.

Group II, claim(s) 56-68, drawn to boron compounds.

The inventions listed as Groups II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: no need for the catalyst of group I is recited in group II.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/23302

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest☐

The additional search fees were accompanied by the applicant's protest.

☒

No protest accompanied the payment of additional search fees.